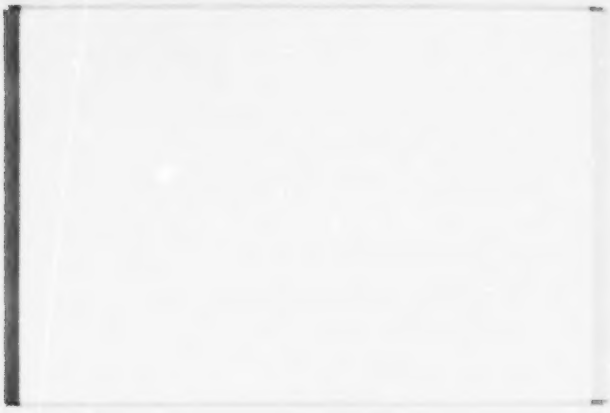
McMASTER UNIVERSITY

HAMILTON, ONTARIO, CANADA



DEPARTMENT OF MATERIALS SCIENCE & ENGINEERING

CONTRACT SERIAL NUMBER 69189-01-ST
DSS REQUISITION NUMBER 23440-6-9189
CONTRACTOR: MCMASTER UNIVERSITY

FINAL REPORT

INVESTIGATION INTO THE DEVELOPMENT OF A PROCESS TO PRODUCE ELEMENTAL SULPHUR FROM THE DIRECT SMELTING OF A SULPHIDE CONCENTRATE

DSS FILE NO. 24ST.23440-6-9189
(1987-1988)

Submitted by

Dr. W-K. Lu
Stelco Professor of Metallurgy
McMaster University
1200 Main St. W.
Hamilton, Ontario
L8S 4L7

to

Dr. J.M. Skeaff
Scientific Authority of the Project
CANMET, EMR
555 Booth Street
Ottawa, Ontario
K1A 0G1

July, 1988

MICROMEDIA

70 pp

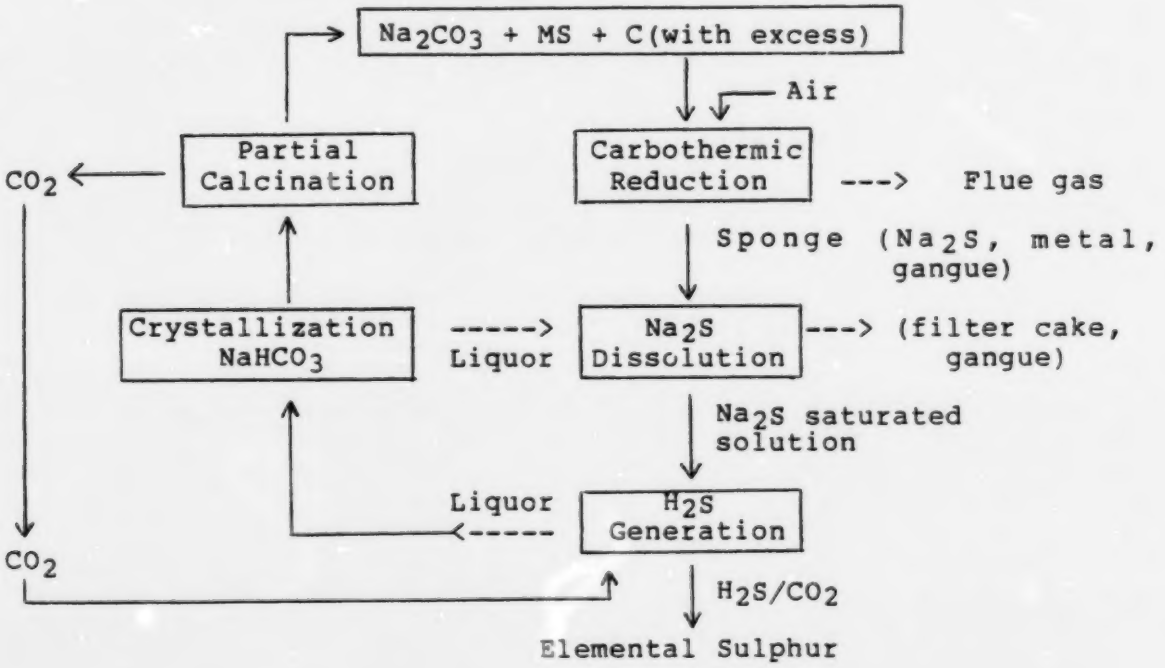
TABLE OF CONTENTS

		Page
1.	Summary	1
2.	Introduction	2
3.	Thermodynamics of Relevant Sulphur-Containing Systems	4
4.	Separation of CaS From Reduced Metals, and Generation of H_2S Through Pyrometallurgy	10
5.	Separation of Calcium Sulphide from Other Products Through Hydrometallurgy	12
6.	Production of H_2S from Na_2S Solution	18
7.	The Process Recommended for Extensive Studies	27
8.	Kinetics of the Generation of H_2S at 24°C	29
9.	Kinetics of the Generation of H_2S and its Dependence on Temperature and Flow Rate of CO_2	43
10.	Conclusions	53
Appendix I:	Carbothermic Reduction of Sulphide Ore by Coal in the Presence of Basic Oxides	54
Appendix II:	Recommended Process for the Conversion of H_2S in H_2S/CO_2 Mixtures to Elemental Sulphur and CO_2 for Recycling	60
Appendix III:	Thermodynamics and Mass Balances of the Treatment of CaS with HCl	65

1. SUMMARY

In the last twelve months, major steps of a new process which have been outlined in our proposal, have been studied. In this process sulphides may be reduced and separated to produce metal and elemental sulphur without the formation of sulphur dioxide. Carbothermic reduction of sulphide ores by coal in the presence of $CaCO_3$ or Na_2CO_3 at a temperature of about 1000°C can be carried out at adequate rate of reaction. In a LB Furnace, all energy required in this pyrometallurgical system may be provided totally by the coal used, with very good energy efficiency.

Soda is recommended as the preferred flux in this carbothermic reduction because we have developed a very efficient way to generate H_2S from Na_2S. The recommended process has the following flow diagram, in which all chemicals are recycled except of course, sulphide and coal.



A new process developed by DOWA Mining Company of Japan is recommended for the step of converting H_2S to elemental sulphur.

2. INTRODUCTION

2.1 Statement of Work in the Contract

"You shall conduct an investigation into the development of a process to produce elemental sulphur from direct smelting of a sulphide concentrate.

Work to be performed shall be generally in accordance with your technical proposal entitled "Investigations into the Feasibility of Direct Reduction and Smelting of Sulphide Ores in a LB Furnace", dated April 15, 1986 and revisions to schedule dated April 27, 1987. Emphasis is to be placed on the separation and recovery of hydrogen sulphide from synthetic calcium sulphide-bearing slags, which will be melted in a plasma furnace.

Work shall emphasize primarily on the following tasks:

Task 3.1 Investigation of H_2S generation from molten slags.

Task 3.2 Recovery of H_2S from the quenched and granulated slags."

2.2 Summary of Original Research Proposal

We propose that direct reduction of copper sulphide concentrate by coal in the LB Furnace with the aim to replace the oxidative roasting in the current practice (i.e., eliminating SO_2 production and its emission to the atmosphere) be investigated. It is anticipated (based on our experience with the ferrous system) that heat from combustion of gases by radiation originated from coal and reduction reactions can be transmitted to the reaction site without oxidizing the metallic phases or CaS and Na_2S.

A controlled amount of basic flux (CaO, Na_2O and carbonates) will be added to the reactor to convert substantially all of the copper and iron to the metallic state. Liquid metal and slag will be tapped from the melting chamber of the LB Furnace. The CaS(Na_2S)-bearing slag will be treated for the recovery of elemental sulphur. The coal/ore ratio will be determined based on the chemical and thermal requirements in the reduction unit.

The following tasks are proposed, to be accomplished over a period of two years, for the purposes of:

(i) the establishment of technical feasibility of this new process; and,

(ii) the establishment of desirable values of process parameters before pilot plant trials.

2.3 Priority of Work Specified in the Contract and the Proposal

The financial support we received was for one year only. There are three major steps in the proposed process:

(i) Carbothermic reduction of sulphide ore in the presence of a basic flux.
(ii) Generation of H_2S from calcium and/or sodium sulphides.
(iii) Conversion of H_2S to elemental sulphur.

As shown in the "Statement of Work" which reflects the wishes of the Scientific Authority of the project, item (ii) has top priority. This report is mainly concerned with the kinetics of generation of H_2S.

Based on what has been reported in the literature* and our own experimental results, Step (i) is unlikely to be critical. Our results which are shown in Appendix I, indicate that soda (which can be recycled) is a more effective flux than limestone.

In converting H_2S to elemental sulphur there are many established processes in the treatment of coke oven gas and natural gas**. However, the new process recently developed by DOWA Mining Company is most suitable for H_2S/CO_2 mixtures. It operates at ambient temperature, atmospheric pressure, and without the use of catalysts. As the absorbent is acidic, it selectively absorbs H_2S and rejects CO_2. For details, see Appendix II.

* Y.K. Rao and S.K. El-Rahaiby, "Direct Reduction of Lead Sulphide with Carbon and Lime; Effect of Catalysts: Part I, Experimental", Met. Trans. B, Vol. 16B (1985), pp.465-475.

R.C. Kerby, "Direct Reduction of Iron and Nickel Sulfides by Calcium Oxide and Carbon Monoxide, With Subsequent Recovery of Elementary Sulfur", Department of Energy, Mines and Resources, Ottawa, Mines Branch (CANMET) Investigation Report IR73-47 (1973), pp.50.

F. Habashi and Raymond Dugdale, "The Reduction of Sulfide Minerals by Hydrogen in the Presence of Lime", Met. Trans. 4 (1973), pp.1865-71.

** W-K. Lu, Editor, "Treatment of Coke Oven Gas", Proc. McMaster Symposium on Iron and Steelmaking, May 1977, published by McMaster University Press.

3. THERMODYNAMICS OF RELEVANT SULPHUR-CONTAINING SYSTEMS

3.1 Lime Enhanced Carbothermic Reduction ($CuFeS_2$-C-CaO)

The carbothermic reduction of chalcopyrite occurs through the gaseous intermediary CO, combined with the solution loss reaction. The reduction by CO as well as by carbon are considered:

$$CuFeS_2 + 2CO_{(g)} + 2CaO \text{ ---> } Cu + Fe + 2CaS + 2CO_{2(g)} \quad (1a)$$

$$K_{1a} = (P_{CO_2}/P_{CO})^2$$

For the reaction with carbon at high temperature,

$$CuFeS_2 + 2C + 2CaO \text{ ---> } Cu + Fe + 2CaS + 2CO_{(g)} \quad (1)$$

$$K_1 = (P_{CO})^2 ,$$

since all other materials are pure solids.

The equilibrium constant for both reactions as a function of temperature are shown in Figure 1. For temperatures of any importance ($T>700^oC$), the equilibrium constant (i.e P_{CO}) is high. The reaction clearly is favorable, and becomes even more favorable as the temperature increases.

3.2 Soda Enhanced Reduction ($CuFeS_2$-C-Na_2O or Na_2CO_3)

For Reaction (2), in the presence of Na_2O, K_2 is very large and increases slowly with increase in temperature

$$CuFeS_2 + 2C + 2Na_2O \text{ ---> } Cu + Fe + 2Na_2S + 2CO_{(g)} \quad (2)$$

However, unlike $CaCO_3$, Na_2CO_3 does not decompose easily, and one must consider Reaction (2a)

$$CuFeS_2 + 4C + 2Na_2CO_3 \text{ ---> } Cu + Fe + 2Na_2S + 6CO_{(g)} \quad (2a)$$

The plots of K_2 and K_{2a} are shown in Figure 2. At about 1000^oK, for pure reactant, and products, the equilibrium P_{CO} for Reaction (2a) is 0.36 atm. As can be seen, K_{2a} increases tremendously with increase in temperature.

3.3 CaS-CaO-H_2O System

Consider the formation of gaseous H_2S from CaS, through reaction with steam

$$CaS + H_2O_{(g)} \text{ ---> } CaO + H_2S_{(g)} \quad (3)$$

$$K_3 = (P_{H_2S}/P_{H_2O}) = P_{H_2S} \text{ for } P_{H_2O} = 1 \text{ atm.}$$

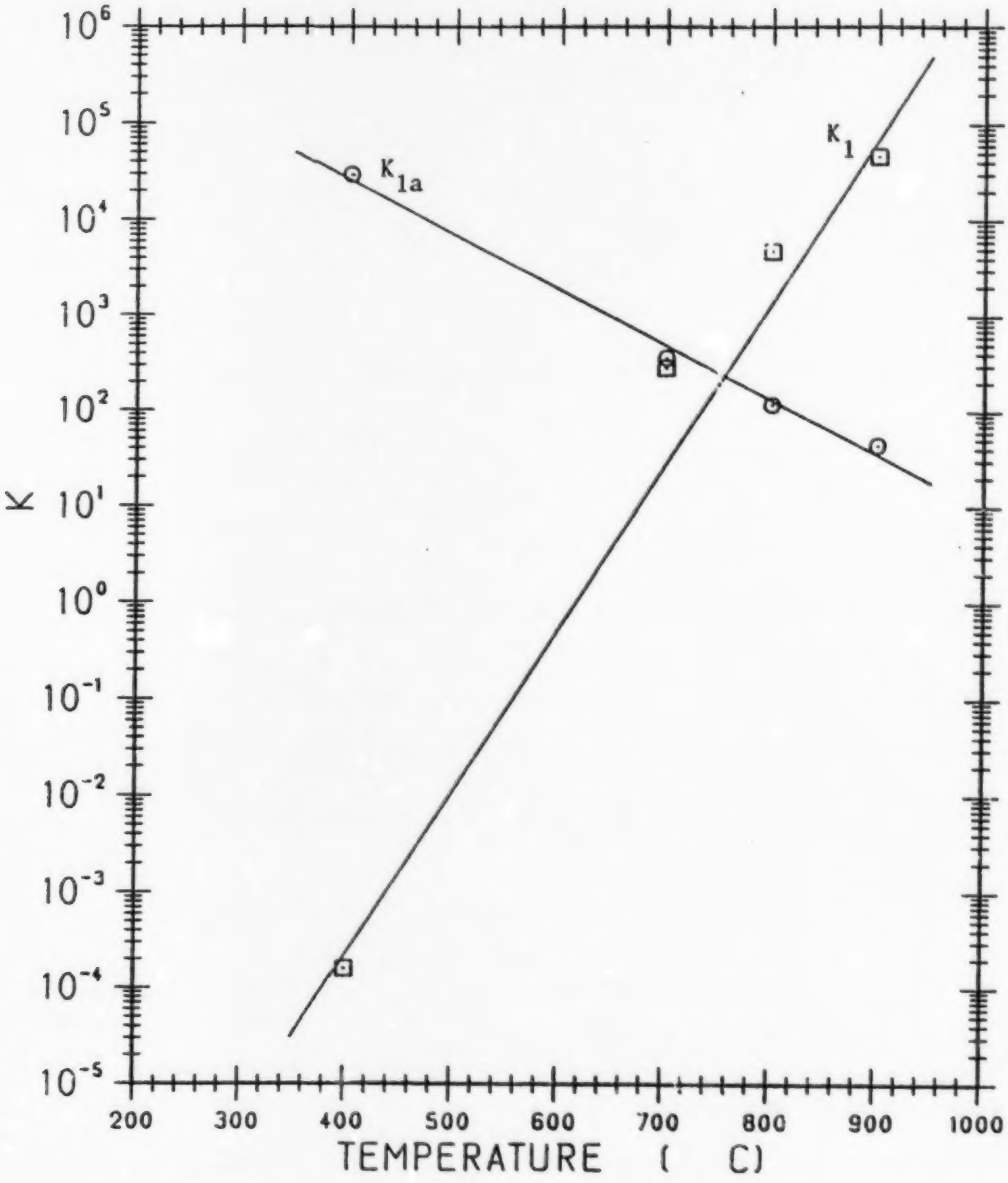


Fig. 1 Lime enhanced carbothermic reduction.

$$CuFeS_2 + 2C + 2CaO \rightarrow Cu + Fe + 2CaS + 2CO_{(g)} \quad (1)$$

$$CuFeS_2 + 2CO_{(g)} + 2CaO \rightarrow Cu + Fe + 2CaS + 2CO_{2(g)} \quad (1a)$$

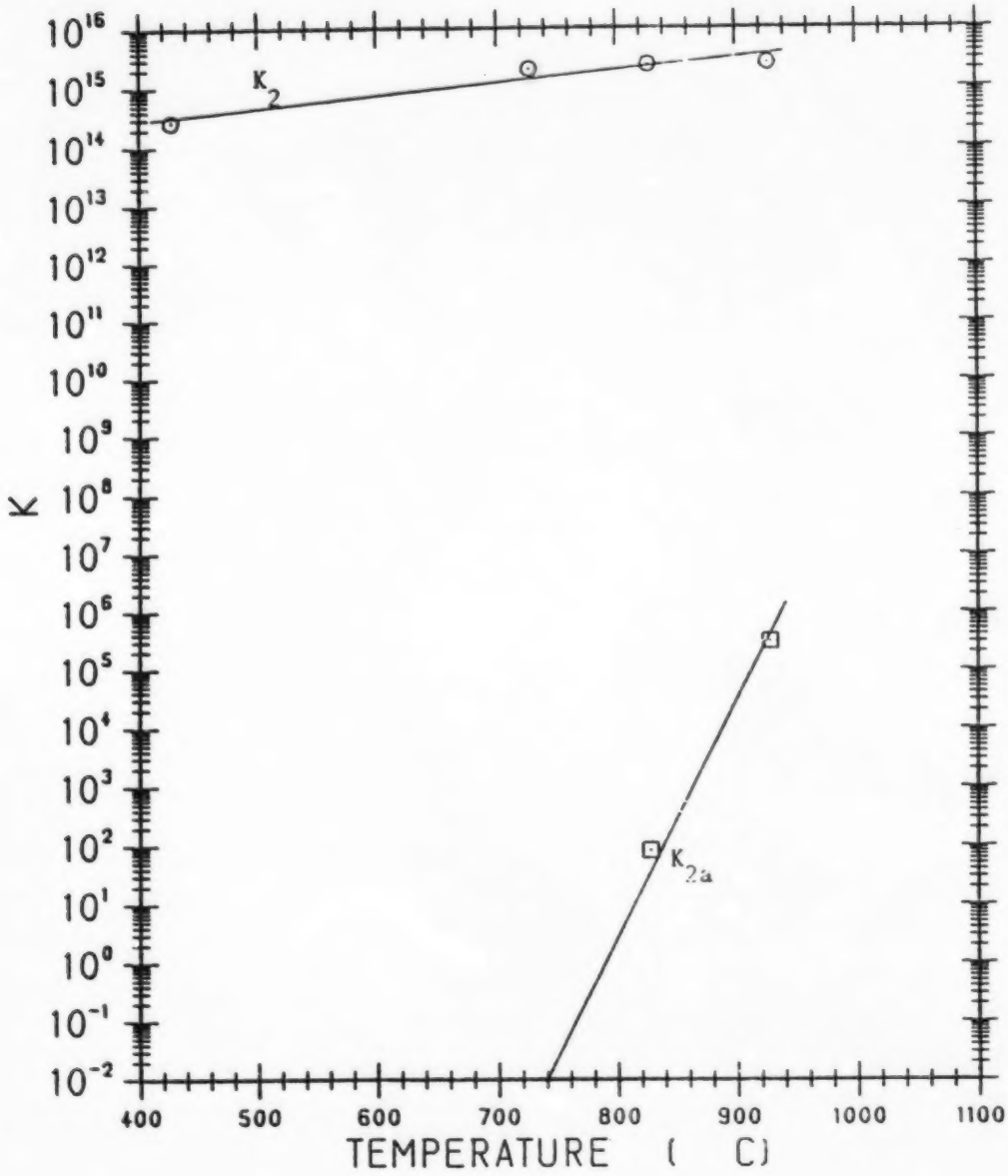


Fig. 2 Soda enhanced reduction.

$$CuFeS_2 + 2C + 2Na_2O \rightarrow Cu + Fe + 2Na_2S + 2CO_{(g)} \quad (2)$$

$$CuFeS_2 + 4C + 2Na_2CO_3 \rightarrow Cu + Fe + Fe + 2Na_2S + 6CO_{(g)} \quad (2a)$$

Variation of K_3 with temperature is shown in Figure 3. It shows that, even at a temperature as high as 900°C, the equilibrium partial pressure of H_2S attainable is too low to be of any significance.

On the other hand, if one considers the more likely case of formation of $Ca(OH)_2$ instead of CaO, then

$$CaS + 2H_2O_{(g)} \text{ ---> } Ca(OH)_2 + H_2S_{(g)} \qquad (3a)$$

the equilibrium constant is increased, but still, even at P_{H_2O} = 1 atm, the H_2S partial pressure attainable is extremely low at 400°K, or 2.6×10^{-2} atm; or $\sim$ 2.6%). The variation of K_{3a} with temperature is also shown in Figure 3.

Thus, any attempt to produce H_2S by treatment of CaO with steam or water is impractical, both at low temperature and high temperature.

3.4 Need for Separation of Reduced Metals From Flux Sulphides Before H_2S Production

Consider the formation of Cu_2S in an environment containing H_2S gas

$$2Cu + H_2S_{(g)} \text{ ---> } Cu_2S + H_{2(g)} \qquad (4)$$

$K_4 = P_{H_2O}/P_{H_2S}$. k_4 is plotted versus temperature in Figure 4. K_4 values are so large, that, even at such low partial pressure of H_2S that are generated by treatment of CaS with steam (Section 3.3), copper is oxidized to copper sulphide. Hence, prior separation of reduced metals (Cu and Fe) from lime sulphide is mandatory, before one attempts to generate H_2S.

If one considers the reaction with steam in presence of Cu (i.e., before the separation step),

$$CaS + 2Cu + 2H_2O_{(g)} \text{ ---> } Ca(OH)_2 + 2Cu_2S + H_{2(g)} \qquad (5)$$

$$K_5 = P_{H_2}/(P_{H_2O})^2 = P_{H_2} \text{ for } P_{H_2O} = 1 \text{ atm.}$$

i.e., Reaction (5) can proceed in the forward direction until P_{H_2} is very high.

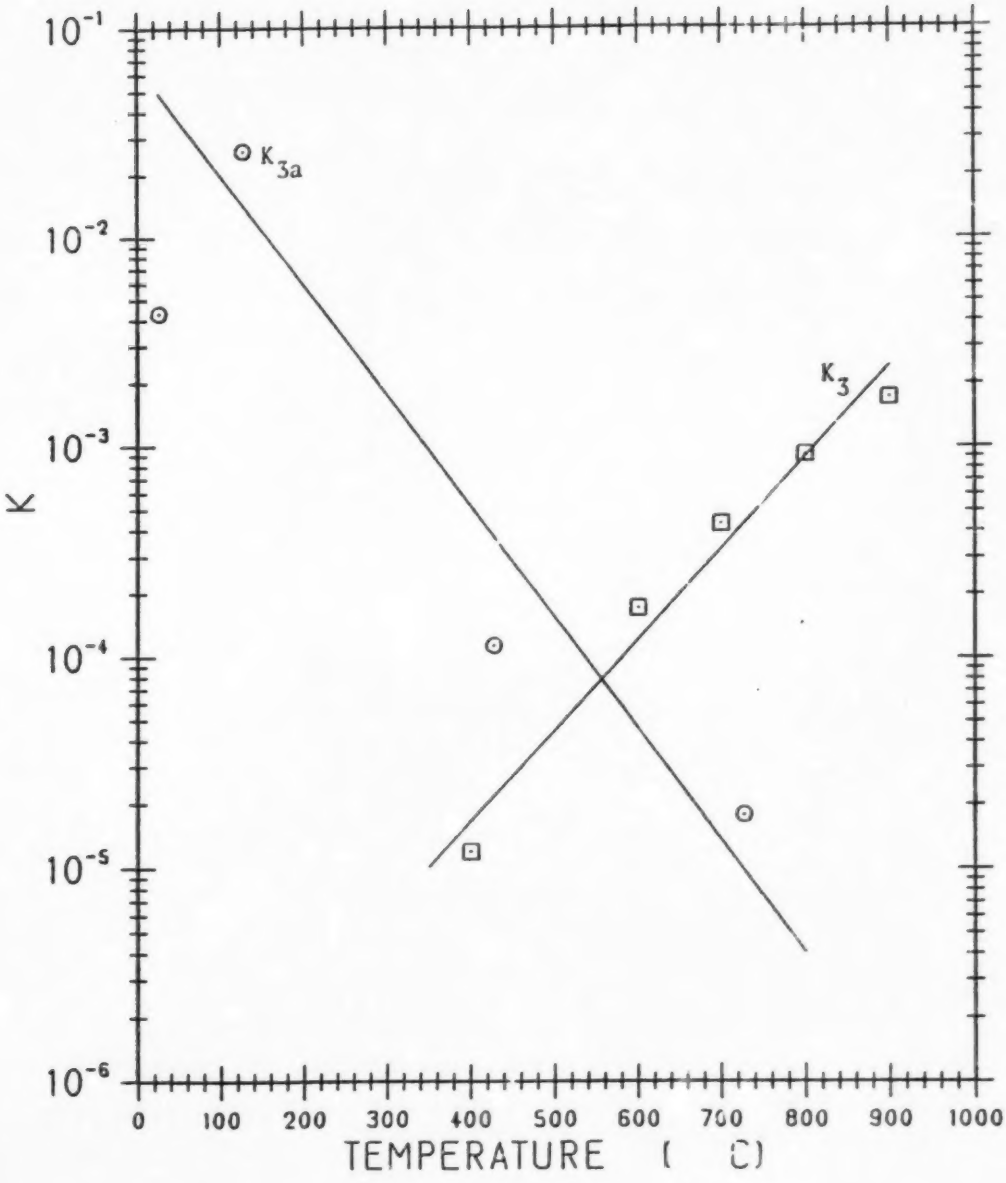


Fig. 3 Equilibrium constant for H_2S generation by steam.

$$CaS + H_2O_{(g)} \rightarrow CaO + H_2S_{(g)} \quad (3)$$

$$CaS + 2H_2O_{(g)} \rightarrow Ca(OH)_2 + H_2S_{(g)} \quad (3a)$$

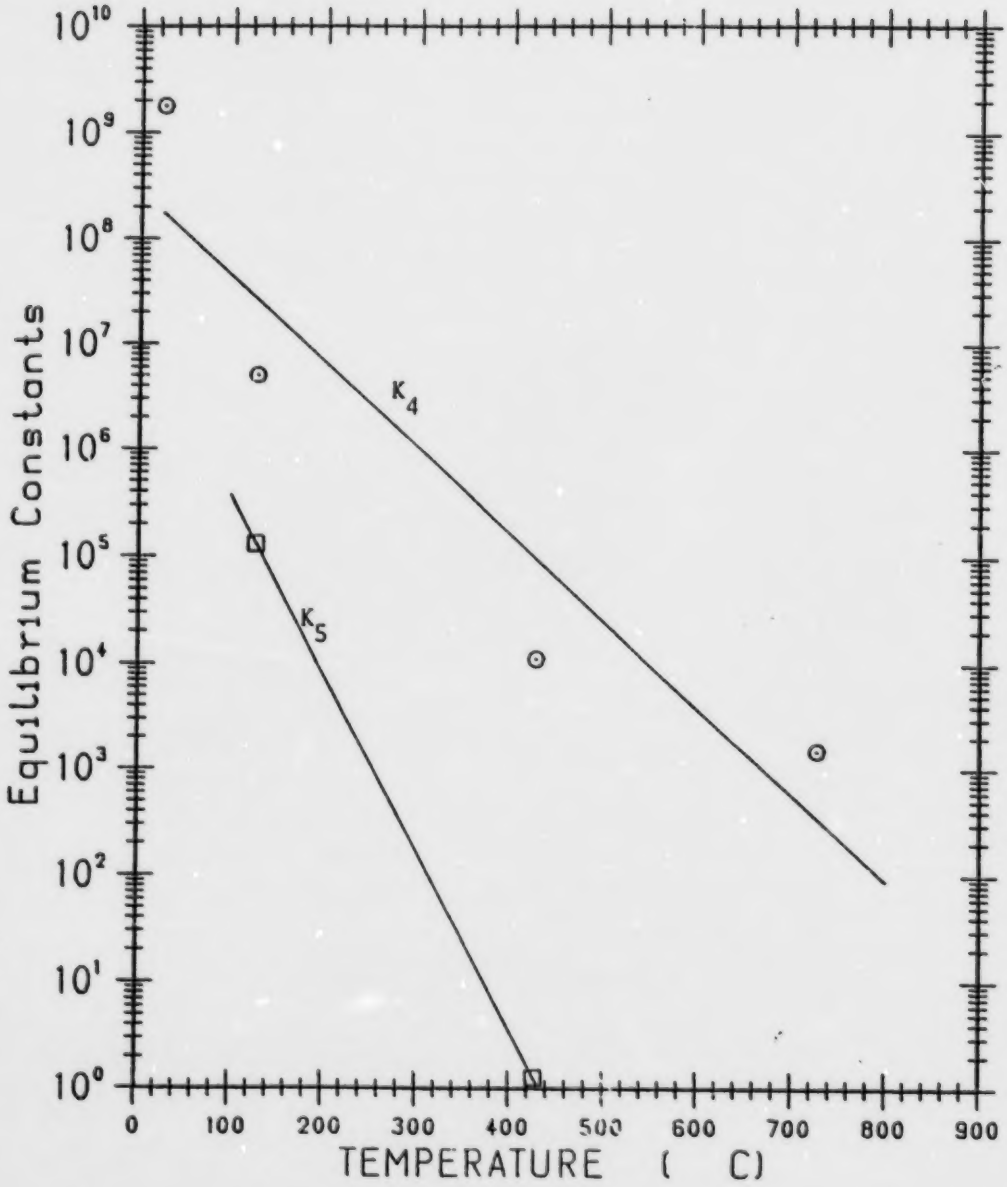


Fig. 4 Equilibrium constant for reactions (4) and (5).

$$2Cu + H_2S_{(g)} \rightarrow Cu_2S + H_{2(g)} \quad (4)$$

$$CaS + 2Cu + 2H_2O_{(g)} \rightarrow Ca(OH)_2 + 2Cu_2S + H_{2(g)} \quad (5)$$

4. SEPARATION OF CaS FROM REDUCED METALS, AND GENERATION OF H_2S THROUGH PYROMETALLURGY

Separation of the reduced metals from calcium sulphide is essential for the following reasons:

(i) for recovery of the metals; and,
(ii) H_2S gas cannot be generated from CaS without re-oxidizing copper to copper sulphide. The relevant thermodynamic data are discussed in section 3.4.

Initially, pyrometallurgical techniques were investigated to implement separation.

4.1 Flux addition and melting

In general, separation by formation of liquid slag and liquid metal layers is a most convenient and practical way. In the present case, unfortunately, CaS is stable in the solid state until high temperature ($T>2500^{o}K$) and at high temperatures, it decomposes. Hence, it cannot be melted without addition of flux (such as silica or alkali chlorides).

We are not aware of any data in the literature about the melting behaviour of CaS in the presence of fluxes. Extensive search of the literature has failed to uncover any system with low melting temperature, in CaS rich slags. It appears that large amounts of fluxes may have to be used. This is undesirable because:

(i) Dilution of CaS would make it less attractive for the production of H_2S from it.
(ii) The volume of CaS produced is at least 8 times that of copper produced. A large flux addition would mean too much volume of material to be handled in the reduction furnace for too little reduction carried.
(iii) The reduction kinetics may be severely hampered by the dilution due to flux addition.
(vi) Even if melting of lime sulphide is possible with alkali chlorides, use of alkali chlorides could have disastrous consequences during the reduction stage.

Due to these limitations, the above approach was given up in the laboratory.

4.2 Treatment with steam or water

One of the methods mentioned in the initial proposal was to generate H_2S from CaS by treatment with steam by the Reaction (3) or (4) (Section 3.3).

Fisher commercial purity grade (C-142) CaS powder was reacted with cold water and boiling water (100°C) in a conical flask covered with a rubber stopper with a glass tube. Very faint rotten egg odour of H_2S was detected. The smell was very weak. When passed over silver nitrate solution, black precipitates of Ag_2S were not formed. All this indicates that the partial pressure of H_2S was extremely small.

Further experimentation was carried out by passing steam from boiling water in a gentle stream of N_2 over a crucible containing CaS powder in the range 800-1000°C.[2] Once again, the partial pressure of H_2S in the exit gas was extremely small. Thermodynamic analysis was carried out later (Section 3.3) which showed that the above results are consistent (the equilibrium constant and hence P_{H_2S} are low at any temperature).

From the above discussion, it is clear that the above approach is impractical and hence, efforts along this line have been discontinued.

5. SEPARATION OF CALCIUM SULPHIDE FROM OTHER PRODUCTS THROUGH HYDROMETALLURGY

Two methods which appeared to be promising are considered. The first one uses acidic medium, and the other uses basic medium.

5.1 Treatment with HCl and Generation of H_2S

In the presence of HCl solution, the following reactions take place:

$$CaS + 2HCl \longrightarrow CaCl_2 + H_2S_{(g)} \quad (6)$$

$$CaO + 2HCl \longrightarrow CaCl_2 + H_2O \quad (7)$$

$$Fe + 2HCl \longrightarrow FeCl_2 + H_{2(g)} \quad (8)$$

Copper is too noble to react with HCl.

All the chlorides are water soluble and hence separation of copper from the rest can be easily carried out. Thermodynamically and kinetically this approach appears to be extremely attractive considering that the separation process and the generation of H_2S can be accomplished in one step. Thermodynamically, the generation of H_2S is not a problem (see Appendix III). The mass balance calculations for a reactor based upon leaching by HCl for the separation and generation of H_2S is also shown in Appendix III. A schematic diagram of the envisioned process is shown in Figure 5.

A system which consists of at least two reactors seems necessary. In the first reactor, the prereduced mixture is treated with HCl solution to result in Reactions (6), (7) and (8). H_2S gas generated in the first reactor is collected for further treatment. The solid mud is mainly copper, excess carbon and other precious metals and gangue. The liquor product out of the first reactor is mainly aqueous $CaCl_2$, which is treated in the second reactor.

The second reactor is for the regeneration of HCl and $CaCO_3$ by use of CO_2 which may be available from the reduction smelting unit. The input for this are (i) the liquor from the first reactor containing $CaCl_2$; (ii) water; and, (iii) CO_2 gas. The output are $CaCO_3$ (according to the reaction $CaCl2 + H2 + CO2 \longrightarrow CaCO_3 + 2HCl$) and liquor containing HCl and unreacted $CaCl2$, which is to be recycled to Reactor I. The thermodynamics and mass balance calculations are listed in Appendix III. In order to regenerate HCl, the necessity of recycling of 16 tonnes of aqueous solution for the treatment of 72 grams of CaS is far from being practical.

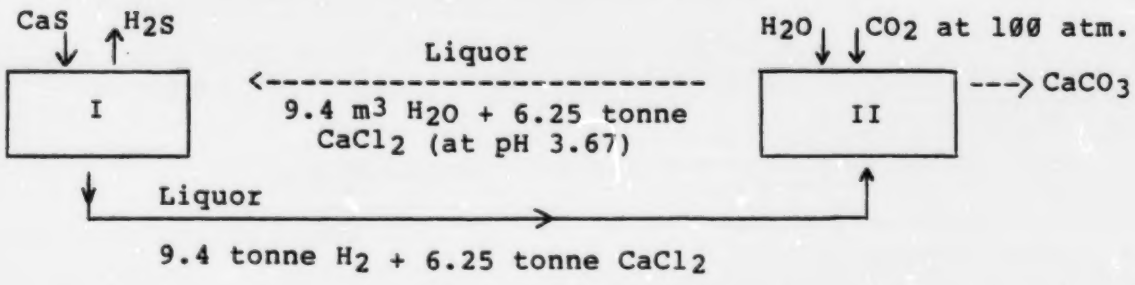


Figure 5 Schematic diagram and mass balance for HCl treatment, per mole of CaS treated.

5.2 Treatment with Base (NaOH)

Considering that the sulphide ions in an aqueous solution are almost completely hydrolized, the reaction through which the separation of CaS from the metallic products and gangue may be implemented is:

$$CaS_{(s)} + OH^-_{(aq)} + H_2O \longrightarrow Ca(OH)_{2(s)} + HS^-_{(aq)} \qquad (9)$$

Since copper is too noble to react with NaOH, filtration would separate sodium sulphide solution from the solids.

(i) Thermodynamic Considerations

For Reaction (9), the equilibrium constant (K_9) is:

$$K_9 = (a_{HS^-})/(a_{OH^-}) = ([HS^-]/[OH^-])\ (\gamma_{HS^-}/\gamma_{OH^-})$$

Due to the lack of data about the activity co-efficients, it is assumed that:

$$K_9 \fallingdotseq [HS^-]/[OH^-] \qquad (9a)$$

The thermodynamic data for aqueous species are tabulated by Barner and Scheuerman*. The K_9 values are shown in Table 1.

From the operational viewpoint in the subsequent step, a high final concentration of [HS-] is desirable. For an assumed final [HS-] concentration of 2 moles/liter, the equilibrium [OH-] concentration calculated from Equation (9a) is also shown in Table 1.

* H. Barnes and R.V. Scheuerman, Handbook of "Thermochemical Data for Compounds and Aqueous Species", John Wiley & Sons, New York (1978).

Table 1: Thermodynamics of Reactions.

T, °K	K_9	[HS-] moles/l	[OH-] moles/l
298	369	2	0.005
373	221	2	0.009

Thus, it is thermodynamically possible to obtain high [HS-] concentration, and to effect separation, provided concentrated NaOH is used.

(ii) Mass Balance Considerations for Design of a Basic Reactor

A system consisting of two reactors is necessary, as shown in Figure 6. In the first reactor, the prereduced mixture is treated with concentrated NaOH. The resultant solution of Na_2S is fed to a second rector, in which it is treated with $NaHCO_3$ and CO_2 gas. To produce H_2S gas for a subsequent production of sulphur.

Consider an operation at 25°C. We assume that equilibrium is achieved at the end of operation in Reactor I. In order to obtain a concentration of Na_2S of 2 molar (4N), $[OH^-]_{final}$ = 0.005 and $[NaOH]_{initial}$ = 4 + 0.005 = 4.005 N.

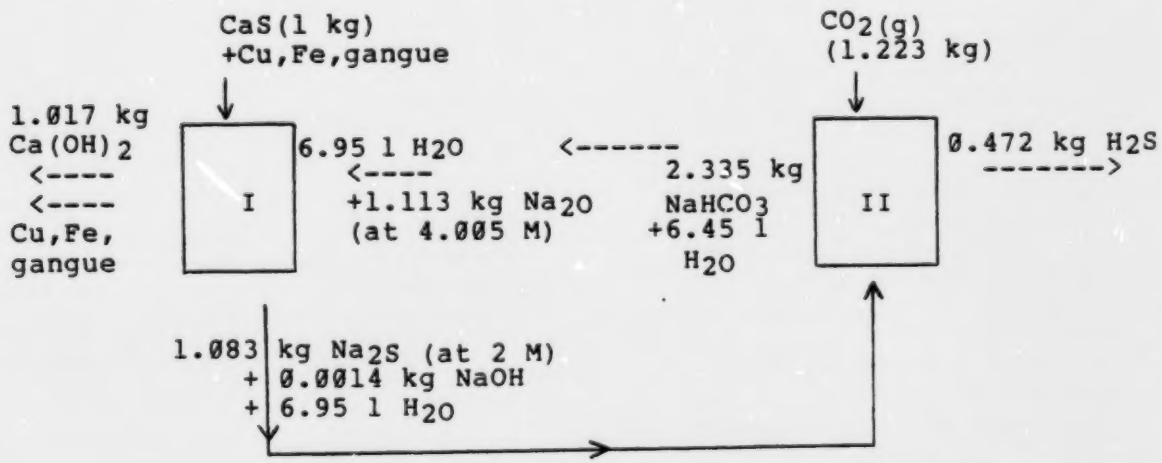


Figure 6 Mass balance for a basic reactor, assuming equilibrium.

REACTOR I

Input

Per kg of CaS in the prereduced mixture,

40/144 x 4.005 = 1.113 kg NaOH at 4.005 M is required

Output

Amount of $Ca(OH)_2$ = 74/72 x 1 kg = 1.017 kg

Amount of Na_2S = 78/72 = 1.083 kg

Amount of NaOH = 0.005 x 40 x 6.95/1000 = 0.0014 kg

REACTOR II

$Na_2S + 2CO_{2(g)} + 2H_2O \longrightarrow 2NaHCO_3 + H_2S_{(g)}$

Amount of $CO_{2(g)}$ required (see reaction above)

= 2 x 44/78 x 1.083, + 0.0014 x 44/40* = 1.223 kg

Amount of H_2S produced = 34/78 x 1.083 = 0.472 kg

Amount of $NaHCO_3$ produced = 2 x 84/78 x 1.083 + 0.0014 x 84*/40

= 2.335 kg

*Due to 0.0014 kg NaOH

(iii) Experimental Study

The experiments described below have been carried out with the following aims: (i) to determine whether the water insoluble CaS can be converted to water soluble Na_2S, in order to separate CaS from metallic products; and, (ii) to determine suitable conditions for efficient conversion.

Reaction in consideration:

$$CaS_{(s)} + 2NaOH_{(aq)} \longrightarrow Na_2S_{(aq)} + Ca(OH)_{2(s)} \qquad (9b)$$

The progress to date has been documented in the following pages.

Experimental Procedure

CaS powders (Fisher C-142, -200#) were treated with NaOH solutions of different concentrations (0.01 N, .1N, 1N, 2N). The experiments documented in this report were carried out at room temperature, in the following manner.

Weighed amounts of CaS were transferred to a conical flask, and volumetric (BDH) solutions of NaOH (or solutions prepared from volumetric solutions, i.e., accurately known pH) were added (80% of stoichiometric quantity) to the flask, shaken and allowed to react for four hours. After the treatment, the resultant mixture was filtered to separate the aqueous part from the solids, washed thoroughly to extract all water soluble material.

The filterate was diluted to 50, 100 or 200 ml, depending on necessity, using volumetric flasks, and tested by the following methods for qualitative and quantitative analysis of the sulphide ions.

- Treatment with lead acetate and silver nitrate.
- Treatment with sodium nitroprusside.
- Quantitative analysis using plasma emission spectroscopy. After examining different possible methods, we think that the plasma emission spectroscopic method in the ultraviolet range (characteristic wave length for S is 0.1806 μm), is a convenient method of analysis from aqueous solutions. From the concentrations of sulphur measured by this method, and the volume of solutions, it was possible to calculate the amount of Na_2S formed by the reaction.

Experimental Results

- Qualitative analysis using Pb acetate and sodium nitroprusside. In all the experiments, a black precipitate of PbS on treatment with Pb acetate, and purpose colorization with nitro prusside were observed (except for 0.01 N NaOH) confirming the reaction between CaS and NaOH.
- Quantitative analysis: From the concentration of S determined from the spectroscopic method, the % conversion of sulphur* (from CaS to Na_2S) is calculated and shown in Table 2.

$$* \text{ \% Conversion} = \frac{\text{weight of sulphur in solution}}{\text{weight of sulphur initially in CaS}} \times 100\%$$

Table 2: Results of treatment of CaS with 80% of stoichiometric requirement of NaOH (by Reaction (9b)) for four hours at room temperature.

Initial [NaOH] N	% Conversion CaS to Na_2S
0.01	0
0.1	20.1
1.0	32.4
2.0	55.2

Conclusions:

- The reaction between CaS and NaOH is slow, but definitely occurs.
- The % of conversion strongly depends upon the concentration of NaOH.

6. PRODUCTION OF H_2S FROM Na_2S SOLUTION

6.1 Thermodynamic Aspects

The principal reaction by which H_2S can be produced from NaHS (from the hydrolysis of Na_2S for which the hydrolysis constant is very high (10^{15}) is:

$$NaHS_{(aq)} + NaHCO_{3(aq)} \text{ ----> } Na_2CO_{3(aq)} + H_2S_{(g)} \qquad (10)$$

The regeneration of $NaHCO_3$ from Na_2CO_3 may be easily carried out by treatment with CO_2 (either in the same reactor or a separate carbonation chamber) through the reaction:

$$Na_2CO_{3(aq)} + CO_{2(g)} + H_2O \text{ ----> } 2NaHCO_{3(aq)} \qquad (11)$$

The equilibrium constant K_{11} for Reaction (11) is:

$$K_{11} = (a_{NaHCO_3})^2/a_{Na_2CO_3} \cdot 1/P_{CO_2} = [NaHCO_3]^2/[Na_2CO_3] \cdot (P_{CO_2})^{-1} \cdot (\gamma_{NaHCO_3})^2/\gamma_{Na_2CO_3}$$

or,

$$[NaHCO_3]^2/[Na_2CO_3] \cdot 1/P_{CO_2} = K_{11} \cdot \gamma_{Na_2CO_3}/(\gamma_{NaHCO_3})^2 = K'_{11}$$

The net reaction ((10) + (11)) in one reactor is:

$$NaHS_{(aq)} + CO_{2(g)} + H_2O \text{ ----> } NaHCO_3 + H_2S \qquad (12)$$

The equilibrium constant for Reaction (12) is:

$$K_{12} \simeq P_{H_2S}/P_{CO_2} \cdot a_{NaHCO_3}/a_{NaHS}$$

or,

$$P_{H_2S}/P_{CO_2} \cdot [NaHCO_3]/[NaHS] = K_{12} \cdot \gamma_{NaHS}/\gamma_{NaHCO_3} = K'_{12}$$

Mai and Babb* measured the phase equilibrium in the above system. K'_{12} (which depends upon the ratio of activity coefficients) varied only from 1.65 to 2.25 over a wide range of composition and P_{CO2}. Hence, for practical purposes, they concluded that K'_{12} can be approximated as a temperature dependent constant. Similarly, K'_{11} also could be approximated as a temperature dependent constant.

* K.L. Mai and A.L. Babb, Ind. Eng. Chem., Vol. 47, 9 (1955), p.1749.

It followed from their measurements that for P_{CO_2} of 0.5 atm. or higher, $NaHCO_3$ (not Na_2CO_3) is the major carbonate in the aqueous solution. For instance, at $[Na^+]$ = 2N, about 98% is $NaHCO_3$ and only 2% is Na_2CO_3, for P_{CO_2} = 1 atm.

The plot of equilibrium values of P_{H_2S}/P_{CO_2} vs. $[NaHS]/[NaHCO_3]$ is shown in Figure 7, for various $[Na^+]$ concentrations, and temperatures up to 65°C. The dashed line represents our calculations at 25°C, for $[Na^+]$ = 2N, i.e., near saturation.

Conclusions

(i) Equilibrium (P_{H_2S}/P_{CO_2} is high enough, provided [NaHS] can be kept high in the solution.

(ii) Thermodynamically, operation at 25°C is more attractive than at high temperature.

6.2 Preliminary Experimental Study of H_2S Generation

From the thermodynamic discussions, it follows that, if $[NaHS]/[NaHCO_3]$ is high, then the equilibrium partial pressure of H_2S is high. So, the initial experiment consisted of passing CO_2 gas through a saturated solution of Na_2S, with no $NaHCO_3$ added (i.e., high [NaHS] and little $[NaHCO_3]$.

(i) Treatment of Na_2S Solution With CO_2 Gas

Fisher reagent grade $Na_2S.XH_2O$ crystals were dissolved in distilled water to make a saturated solution. High purity CO_2 gas at a flow rate of 100 ml/min (STP) was passed through the solution maintained in a gas wash bottle. The exit gas passed through freshly prepared alkaline sodium nitroprusside solution and then through silver nitrate solution for detection of H_2S gas.

No purple coloration of sodium nitroprusside, nor formation of any black silver sulphide precipitation was observed even after one hour, indicating that H_2S generation was below the detectability limit.

This means that the reaction is kinetically slow in the absence of dissolved bicarbonate ions.

(ii) Treatment of Na_2S With $NaHCO_3$

(a) Preliminary Experiments

Saturated solution (prepared from BDH reagent grade) of $NaHCO_3$ was added to saturated solution of Na_2S in a beaker. Evolution of a gas with a strong rotten smell took place. A filter paper dipped in freshly prepared alkaline sodium

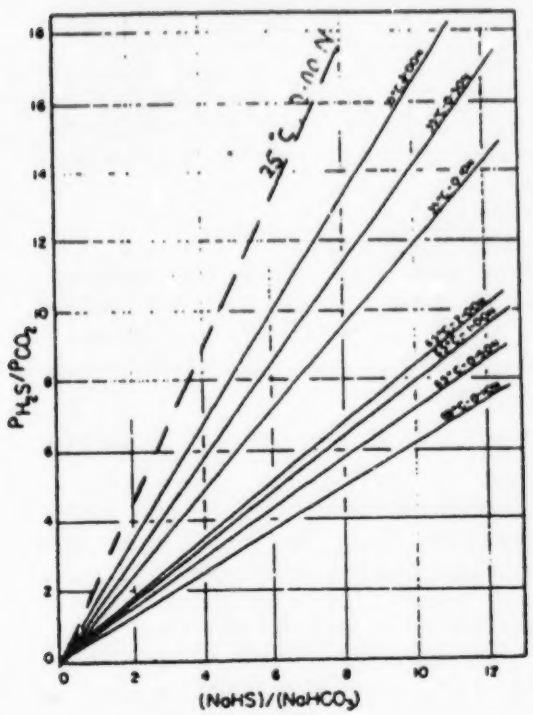


Figure 7 Partial pressure ratio of hydrogen sulphide and carbon dioxide over sodium hydrosulphide-bicarbonate solutions.

nitroprusside, held above the beaker, turned purple, confirming that the gas generated was H_2S.

(b) Determination of H_2S Evolution Rate by Gravimetry

If H_2S evolution occurs by Reaction (10), then by stoichiometry 34 grams H_2S is liberated per mole of Na_2S reacted. This offers a possibility of continuously studying the reaction rate by measuring the weight change. However, corrections are necessary, due to the evaporation of H_2O from the aqueous solution.

Two saturated solutions of $NaHCO_3$ (37 grams of $NaHCO_3$ in each) were prepared in identical beakers (i.d. 3.87 cm and 3.88 cm), to one of which a small amount (2.750 grams) Na_2S was added which dissolved completely. The weight change of these as well as another beaker (i.d. 3.84 cm) containing distilled water, was measured for various times, up to 42 hours.

Figure 8 shows the plot of weight change per unit area vs. time for the three solutions. At any given time, the rate of water evaporation in the case of $NaHCO_3$ saturated solution is lower than in the case of distilled water. But the solution which contains a small amount of H_2S shows a different behaviour. At first, the weight loss is faster than that of distilled water, and then becomes lower.

The activity of H_2O is lowered by the addition of the solutes $NaHCO_3$ and Na_2S. This means that the vapour pressure of H_2O (and hence the rate of evaporation of water) should have been the lowest in the case of the solution containing $NaHCO_3$ as well as Na_2S. Since the amount of Na_2S is small in comparison with $NaHCO_3$ (molar ratio 1:13.5) the rate of water evaporation of H_2O may be approximated by that from the solution containing only $NaHCO_3$. The % conversion to H_2S, calculated from the difference between curve (2) and curve (3) is shown in Figure 9.

Clearly, under the conditions used in the above experiment, the rate of conversion to H_2S is low, and at least 5 hours were necessary to achieve 50% conversion.

The possible reasons for the low rate of conversion to H_2S could be: (a) difficulty of nucleation of the H_2S bubble; (b) low partial pressure of CO_2.

(c) Experiments to Improve Nucleation

A saturated solution containing Na_2S and $NaHCO_3$ was made and poured into two identical beakers. In one beaker, porous fireclay bricks were put to act as nucleation sites. The weight loss vs. time was again measured and compared. The results are shown in Figure 10. There was virtually no improvement in the conversion rate, which indicates that nucleation is not the rate-limiting step.

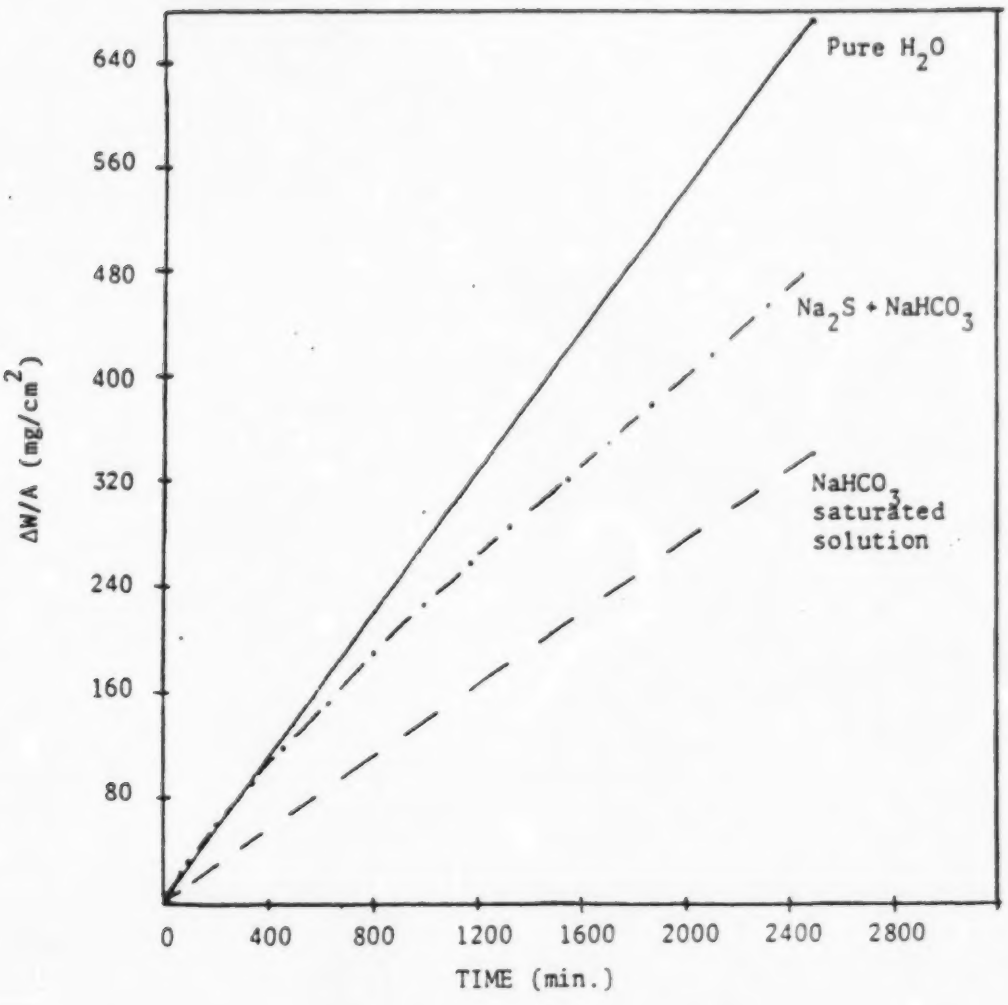


Figure 8: Treatment of Na_2S by $NaHCO_3$ to generate H_2S (25°C).

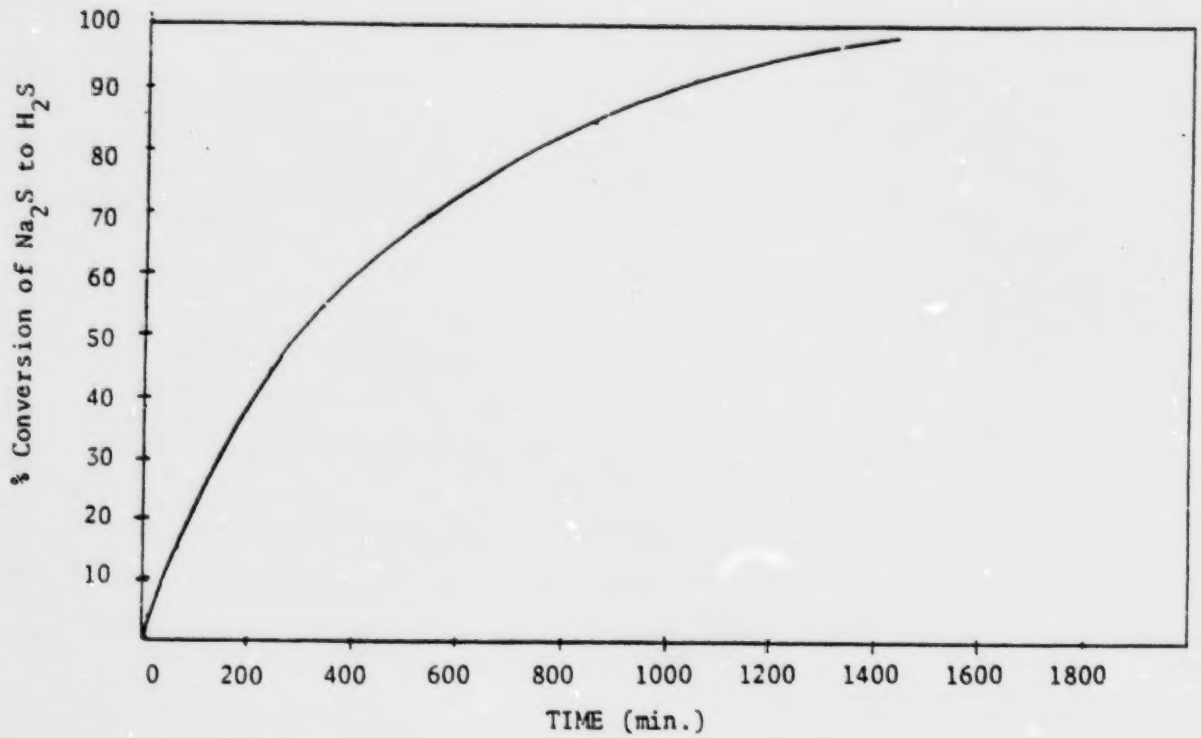


Figure 9: H_2S conversion rate at 25°C by gravimetry.
Reaction: $Na_2S + 2NaHCO_3 \rightarrow 2Na_2CO_3 + H_2S_{(g)}$

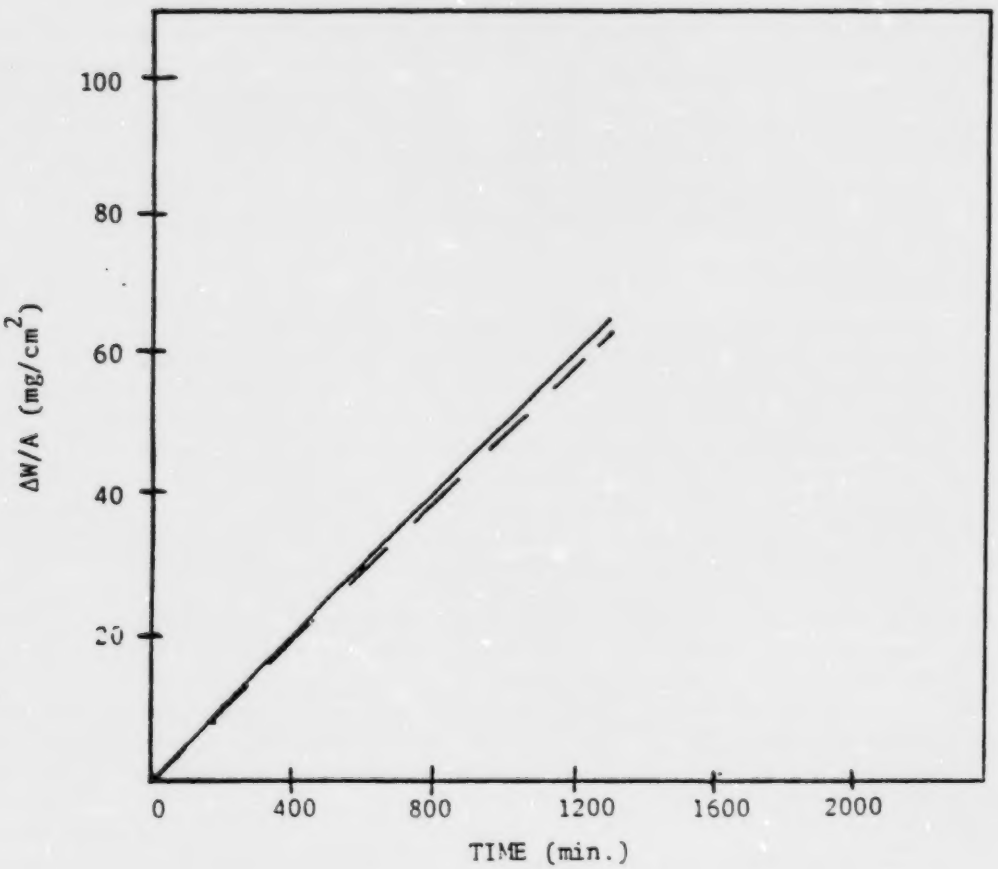


Figure 10 Effect of nucleating agent.
Solid line: No fireclay.
Broken Line: Porous fireclay nucleating agent.

(d) Difficulty in Production of H_2S Without CO_2 Gas

A thermodynamic argument can be put forward to account for the slow production of H_2S gas, from Reaction 10. In air, P_{CO_2} = 2×10^{-4} atm. For such a low value of P_{CO_2}, unfortunately, Reaction (11) proceeds in the reverse direction. Taking K_{11} = 0.117 at $[Na^+]$ = 2N, from Mai's data, one obtains:

$$[NaHCO_3] = 4.7 \times 10^{-3}, \quad [Na_2CO_3] = 0.998$$

In Reaction (10), through which H_2S production was intended, $NaHCO_3$ is reactant, Na_2CO_3 is a product. So, the effect of reversal of Reaction (11) (which is fast) is to decrease the equilibrium value of P_{H_2S}, drastically. Further, by mass action law, the kinetics should be expected to be slow.

6.3 Treatment of Na_2S Solution with $NaHCO_3$ and CO_2 Gas

(i) Experimental Procedure

A weighed amount (11.7 grams) of reagent grade $Na_2S.xH_2O$ was dissolved in 25 ml of water, so that some amount of undissolved Na_2S crystals were left (in order to keep the concentration of Na_2S high for some time during the course of the experiment). Similarly, an aqueous solution (50 ml) containing 3.6 grams of $NaHCO_3$ was prepared and transferred to a gas-washing bottle 4 cm i.d.), along with the Na_2S solution. Flow of CO_2 gas, through the bottle, controlled by a Matheson mass flow controller (flow rate = 118 ml/min; STP), was started an hour prior to the experiment, in order to flush out all air. A dispersion tube distributed CO_2 gas in the form of fine bubbles to the reaction liquid. The exit gas then passed through alkaline sodium nitro prusside and aqueous silver nitrate solution to detect H_2S gas before re-exiting into a fumehood. CO_2 was passed through the aqueous reaction solution for 2 hours, after which the solution was transferred to a volumetric bottle and diluted, finally to 25 liters.

Due to the hygroscopic nature of Na_2S, the sulphur content could not be calculated from the initial weight. Therefore, another standard solution was made which contained exactly 1/5 of the weight of $Na_2S.xH_2O$ in the reaction mixture, in 5 liters of solution.

The concentration of sulphur was measured in the standard (unreacted) solution, as well as the one which reacted for two hours by emission spectroscopic method. From the measurements on standard solution, the initial sulphur content became known, and the % conversion to H_2S was calculated as:

$$\frac{\text{Weight of sulphur in solution after reaction}}{\text{Weight of sulphur initially in the solution}}$$

(ii) Results of the Experiment

(a) For the first few minutes (about 5-10 minutes) there was no indication of any reaction between NaHS (from Na_2S) and $NaHCO_3$. We believe that this was because of low initial concentration of $NaHCO_3$, which increased later on due to carbonation. After this initial period, the sodium nitroprusside turned violet and silver nitrate into black precipitates of Ag_2S, and the exit gas had strong H_2S odour, confirming the generation of H_2S.

The important analytical results after reaction for 2 hours are given below:

% Conversion to H_2S	=	59
Average value of (P_{H_2S}/P_{CO_2})*	=	0.08
Average % H_2S in exit gas*	=	7.5
Gas residence time**	=	1 sec.

* Calculated from the total # of moles of H_2S generated and # of moles of CO_2 passing in 2 hours.

** Time for gas bubbles to travel through liquid column of 10 cm depth, by visual observation.

It is noted that the % conversion of 59% is sufficiently high to be termed "promising". Also important from the viewpoint of the process, after only 1 second contact time, the time averaging of % H_2S is already 7.5%. With increased gas-liquid contact time, the (P_{H_2S}/P_{CO_2}) ratio and hence, % H_2S in gas should be higher because the system is far from equilibrium.

7. THE PROCESS RECOMMENDED FOR EXTENSIVE STUDIES

For economic winning of metal and elemental sulphur from a sulphide by carbothermic reduction, based on what we know today, Na_2CO_3 appears to be more promising than limestone, as the reagent to provide the basic oxide. The flow chart is given in Figure 11.

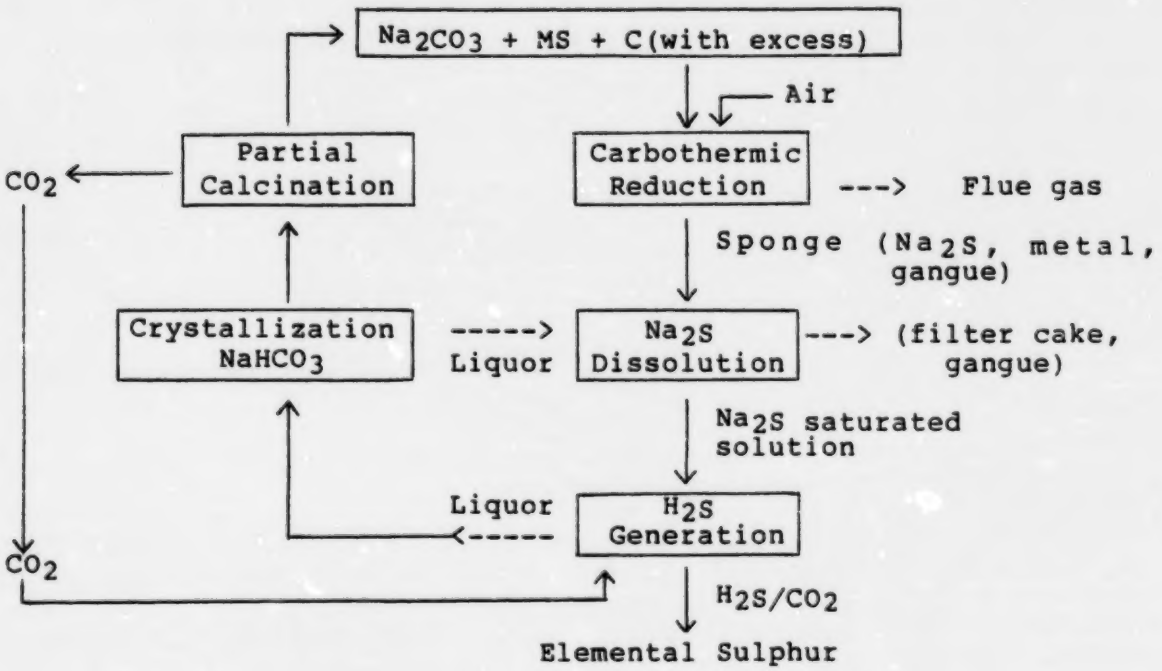


Figure 11 Schematic flow chart of the process to be further studied.

The experimental results described so far have led to the conclusion that it is possible to generate H_2S of sufficiently large partial pressure for sulphur generation, through the reaction of Na_2S with $NaHCO_3$ in the presence of CO_2 gas. However, it is noted from the thermodynamic calculations, that the $(^PH_2S/^PCO_2)$ ratio is much smaller than the equilibrium value. In all the existing technologies for sulphur manufacture, the higher the H_2S content in the gas, the more suitable the gas is. So, it is very important to determine the optimum conditions for H_2S generation.

The major variables identified to be studied are:

(i) Initial concentrations of Na_2S (NaHS), $NaHCO_3$ and P_{CO_2}.

(ii) Time of reaction.

(iii) Temperature of reaction (initially 24°).

It should be noted that the only consumables are the sulphide and coal, which provides all the energy required.

For the conversion of H_2S to elemental sulphur we would recommend the DOWA/NKK Process; for details see Appendix II.

8. KINETICS OF THE GENERATION OF H_2S AT 24°C

8.1 Aim of Experiment

(i) To establish the experimental techniques and also the method of measurement of reaction extent.
(ii) Quantitative characterisation of the reaction (conversion to H_2S) as a function of time, for an initially concentrated solution of Na_2S.
(iii) To study the effect of CO_2 flow rate.

8.2 Experimental Procedure

A large amount of Fisher scientific grade $Na_2S\ XH_2O$ were weighed and dissolved in distilled water to obtain a concentrated master solution. Similarly, a concentrated aqueous soda solution was prepared.

A diagram of the experimental set up is shown in Figure 12. It consists of a series of three glass reactors in series. CO_2 gas of Coleman instrument grade whose volume flow rate is accurately controlled is delivered from a Mathesson controller to the reactor assembly. The reacted gas passes through bubblers containing alkaline sodium nitroprusside, and silver nitrate, or is directly delivered into the fumehood exit.

About an hour before the start of the experiment, CO_2 flow at high rate was begun in order to purge out air from the reactor assembly. Unless described otherwise, only the first reactor was used, with the other two remaining empty. CO_2 is delivered from the dispersion tube in the form of fine bubbles (<2 mm in size).

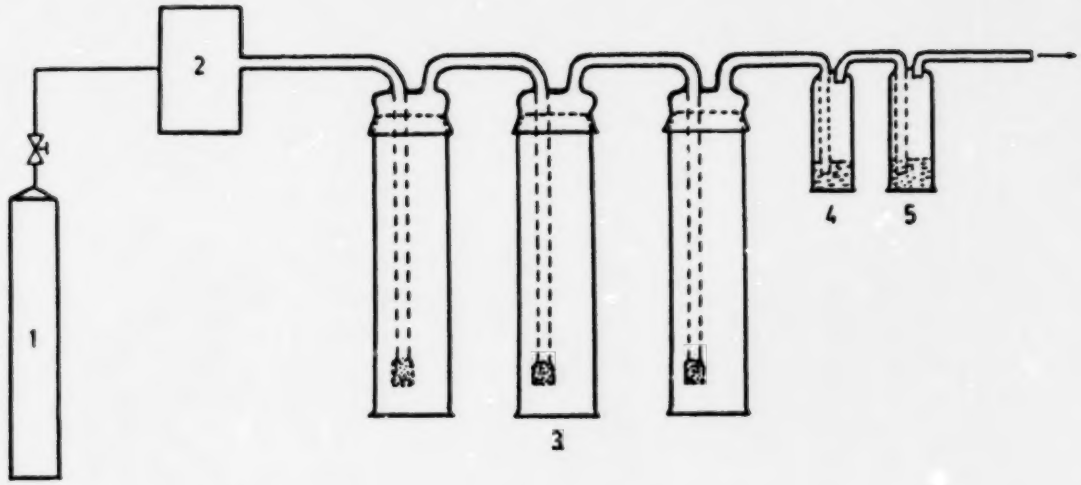
When only one reactor was used, 50 ml of Na_2S solution was mixed with 100 ml $NaHCO_3$ solution and transferred to the reactor. After the predetermined time of reaction CO_2 flow was stopped. The remaining solution was immediately transferred to a volumetric flask and diluted to 1 liter, so that any continuation of the reaction would be minimized. The solution was further diluted suitably (10 or 50 times), for titration and plasma emission spectroscopy. This also had the required effect of slowing down the reaction to an imperceptible level.

8.3 Determination of the Reaction Extent

Two methods of measurement were proposed:

(i) Plasma emission spectometry
(ii) Red-ox titration after absorbing H_2S generated in ammoniacal $ZnSO_4$.

While it is a pleasure to note that the generation of H_2S by the said method is fast, it resulted in problems regarding accuracy of the above methods (described below). This problem had to be overcome through modifications as below.



1 - CO_2 cylinder
2 - Mass flow controller
3 - Reaction bottles
4 - Sodium nitroprusside
5 - $AgNO_3$ solution

Fig. 12 Experimental set-up for H_2S generation.

Since we start with a large amount of Na_2S in the reactor (5-10 gm), due to the fast kinetics of the reaction (described in the results) a large amount of H_2S is liberated. When dilute solution of $ZnSO_4$, was used, all of it was consumed in a short time. So, a concentrated solution of ammoniacal $ZnSO_4$ has to be used. Attempts to do so failed, because, in concentrated solution, unfortunately, $Zn(OH)_2$ precipitated. When a large amount of dilute $ZnSO_4$ was attempted, the volume of the solution, and hence, the pressure head through which the gas had to be passed was too high.

In order to overcome this difficulty, the iodometric titration was performed on the reacted $Na_2S+NaHCO_3$ solution, and the amount of sulphur remaining in the system was measured.

8.4 Experimental Results

(i) Degree of reaction vs. time

Figure 13 shows the conversion to H_2S as a function of reaction time, for CO_2 flow rate of 160 ml/min. at room temperature. The initial concentration of Na_2S in the solution was 0.45 M.

The reaction was studied in the range from 15 minutes to 4 hours. It is apparent from this figure that a high degree of conversion is achieved in a relatively short time. About 75% conversion of Na_2S solution to H_2S is achieved in less than an hour of reaction time; about 40% in 30 minutes.

(ii) Variation of reaction rate with time

From the data, one can obtain the time average of reaction rate ($\Delta X_S/\Delta t$) in different time intervals. Such an analysis is made and shown in Figure 14. The vertical slabs show the mean reaction rate within each time interval. A smooth curve for the rate is drawn in the same figure.

In most isothermal reacting systems, in the absence of changes in externally imposed conditions, one expects the highest rate of reaction in a batch reactor at the beginning and the rate of reaction usually decreases with time. This is often because, concentrations of the reactants are decreasing. In contrast, in the present system,

(a) The reaction rate is slow initially.
(b) The rate increases after some time to a peak value (dX/dt 0.02/min.) somewhere between 15-30 minutes of reaction time in this set of experiments (at room temperature).
(c) The rate continuously decreases after about 30 minutes, and after about 90 minutes, is very slow. It is important to note that by the latter time, the extent of conversion (%X) is already 85%.

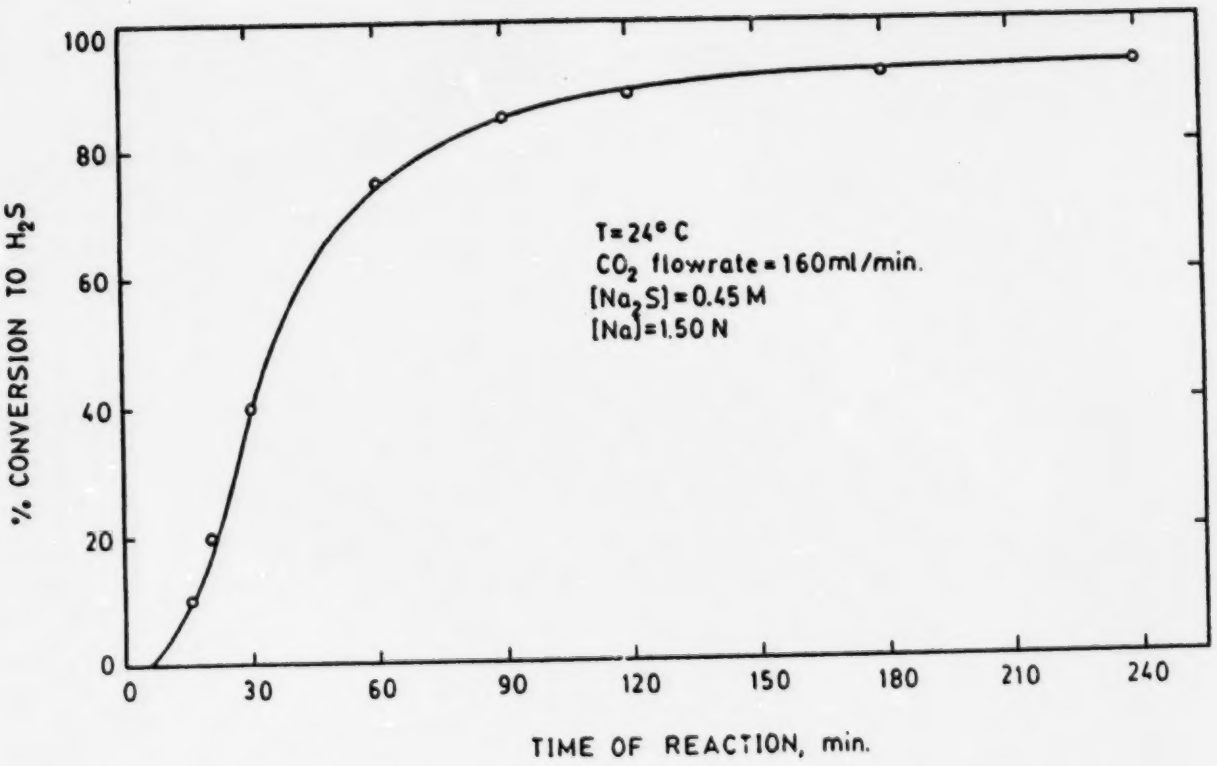


Fig 13 Conversion of Na_2S to H_2S by reaction with CO_2 in the presence of $NaHCO_3$.

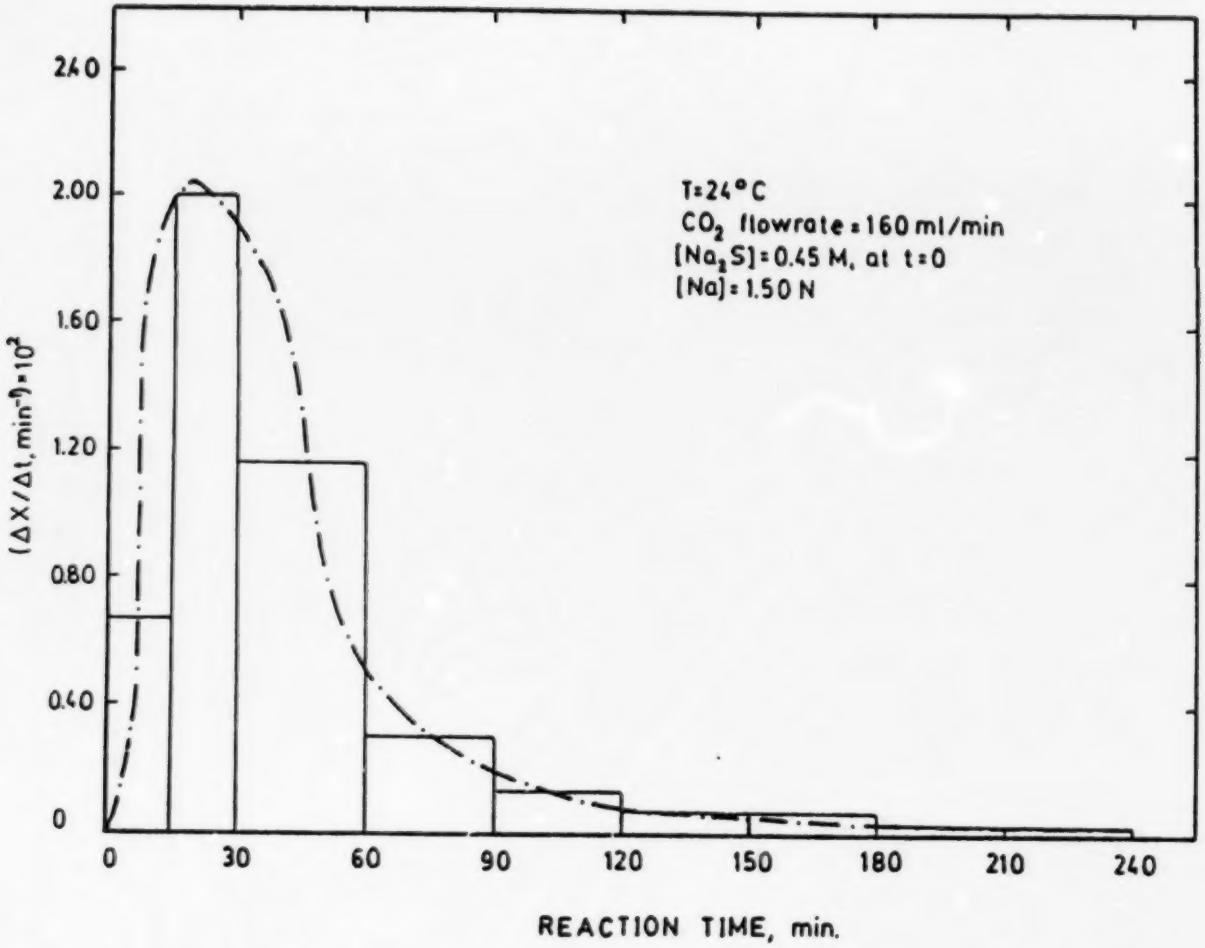


Fig. 14 Variation of reaction rate with time.

There were other indications that the initial reaction rate was low. The experiments at the longer reaction times (t>60 min) were performed before the ones at short duration. In these experiments, it was noted that in the first 5-10 minutes, the odour of H_2S in the exiting gas was weak. Further, when the gas was passed through alkaline sodium nitroprusside and silver nitrate solutions, for about 5-10 minutes, the colour of the nitroprusside did not turn violet and also, no black precipitates or Ag_2S were observed. (Initially, it was thought that this may be because of some leak, but there was no indication of any leak). In all the cases, after this initial period, the colour of nitroprusside began changing to violet; black ppt of Ag_2S began to form; and the odour of H_2S was strong.

8.5 Possible Cause of Low Initial Rate

We believe that we have determined the cause of low initial rate. An experiment performed with a large amount of reactant (100 ml Na_2S + 200 ml $NaHCO_3$ solution) provided the clue. Because of the large volume of liquid, a series of three reactors had to be used. It was visually observed that in the initial period, there was a marked difference in the rate of bubbling of CO_2 between the first reactor and the third one. The extent of bubbling in the second reactor was, of course, in between. After about 15 minutes, the difference had decreased perceptibly, i.e. the rate of bubbling in the second and third reactor had perceptibly increased.

The initial difference in the bubbling rate can only mean one thing: CO_2 was being consumed in the reaction mixture, without generating H_2S in this period.

Sodium bicarbonate loses CO_2 during preservation over long period, and more so after the preparation of aqueous solution. In air, $P_{CO2} \sim 2 \times 10^{-4}$ atm. For [Na+] = 2N, at equilibrium in air, $[NaHCO_3] \sim 5 \times 10^{-3}$, $[Na_2CO_3] \sim 0.998$, i.e. the aqueous soda solution would have decomposed into Na_2CO_3 almost completely. So, in the reaction mixture, in the initial period, CO_2 is used up in generating $NaHCO_3$. Initially rate of H_2S generation is low because the concentration of the reactant $NaHCO_3$ is low.

The calculation of the order of magnitude of time it takes to reach saturation of CO_2 (i.e. equilibrium $NaHCO_3$ concentration) can yield some insight. At saturation, in 100 ml aqueous solution, there would be $\sim$ 0.1 mole of $NaHCO_3$. For initial $[NaHCO_3] = 5 \times 10^{-3}$, at CO_2 flow rate of 160 ml/min., if one assumes that all CO_2 is used up in carbonation, mass balance calculations yield that about 8 minutes are required to reach saturation. One notes that the time required to attain the peak rate of H_2S generation (Figure 14) is of the same order of magnitude ($\sim$15 minutes).

8.6 Effect of Prebubbling of CO_2

A set of experiments was performed in the same way as before, except for the following difference. After flushing the apparatus with CO_2 for an hour, only 100 ml of $NaHCO_3$ (i.e. no Na_2S) was transferred to the reaction bottle and CO_2 was bubbled (at 160 ml/minute) through it for 20 minutes. After this pre-bubbling, 50 ml of Na_2S solution was transferred to the reactor. After this, the reaction was carried out for 15 and 30 minutes, and finally the concentration of remaining sulphur was measured.

Table 3 shows the effect of prebubbling on the extent of conversion. It is obvious that pre-bubbling improved the reaction kinetics as evidenced by the conversion and mean $\%H_2S$ in the gas. Thus, the above experiment confirms that the initial low reaction rate is indeed due to the low initial concentration of $NaHCO_3$. It is important to note that, if saturated $NaHCO_3$ were used, the reaction kinetics would always be faster than shown in Figure 14.

8.7 H_2S Content in Exit Gas

In any of the existing technologies for the production of elemental sulphur it is desirable to have as high H_2S content as possible. For many of them to be operative, it is necessary that the gaseous, H_2S content be higher than a certain minimum value. From this point of view, it is important to calculate the H_2S content in the gas exiting from the experimental set up. From the measured values of % conversion, the mean H_2S content in the outgoing gas was calculated by mass balance, taking into account the following:

(i) Incoming CO_2 flow rate is constant, at 160 ml/min., throughout.

(ii) 2 moles of CO_2 are consumed per mole of H_2S generated ($Na_2S+2H_2O+2CO_2 \rightarrow 2NaHCO_3+H_2S(g)$). Therefore, the amount of CO_2 in the outgoing gas can be calculated by mass balance.

(iii) Actually, CO_2 is also consumed, during carbonation of Na_2CO_3, in the initial period. Although this decreases the number of moles of CO_2 considerably, this is neglected in the calculation because we have no knowledge about the rate of carbonation.

Figure 15 shows the mean $H_2S\%$ in the exit gas. The mean (H_2S/CO_2) is in Figure 16.

It has to be pointed out that, in these experiments, the liquid column through which the gas passes is less than 15 cm long and contact time is less than 1 sec. It is reasonable to assume that at least 10% H_2S is essential in the gas phase, to produce elemental sulphur. It is seen from Figure 14, that for about an hour (or till about 75% conversion) the H_2S content in the exit gas is high enough to facilitate sulphur production.

Table 3: Effect of Prebubbling of CO_2

Reaction Time	No Prebubbling		Prebubbling	
	% X	Average % H2S in exit gas	% X	Average % H2S in exit gas
15	9.6	7.1	14.1	10.8
30	39.6	15.8	52.2	21.9

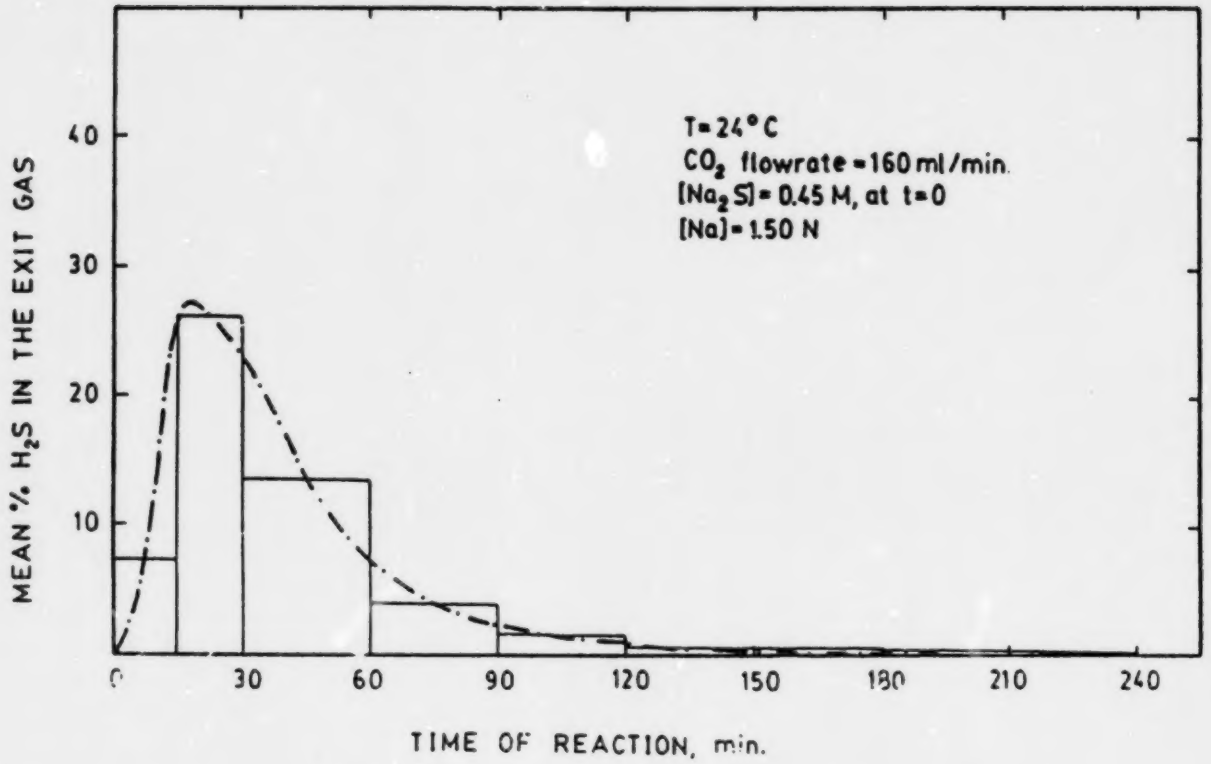


Fig. 15 Variation of the H_2S content in the exit gas with reaction time.

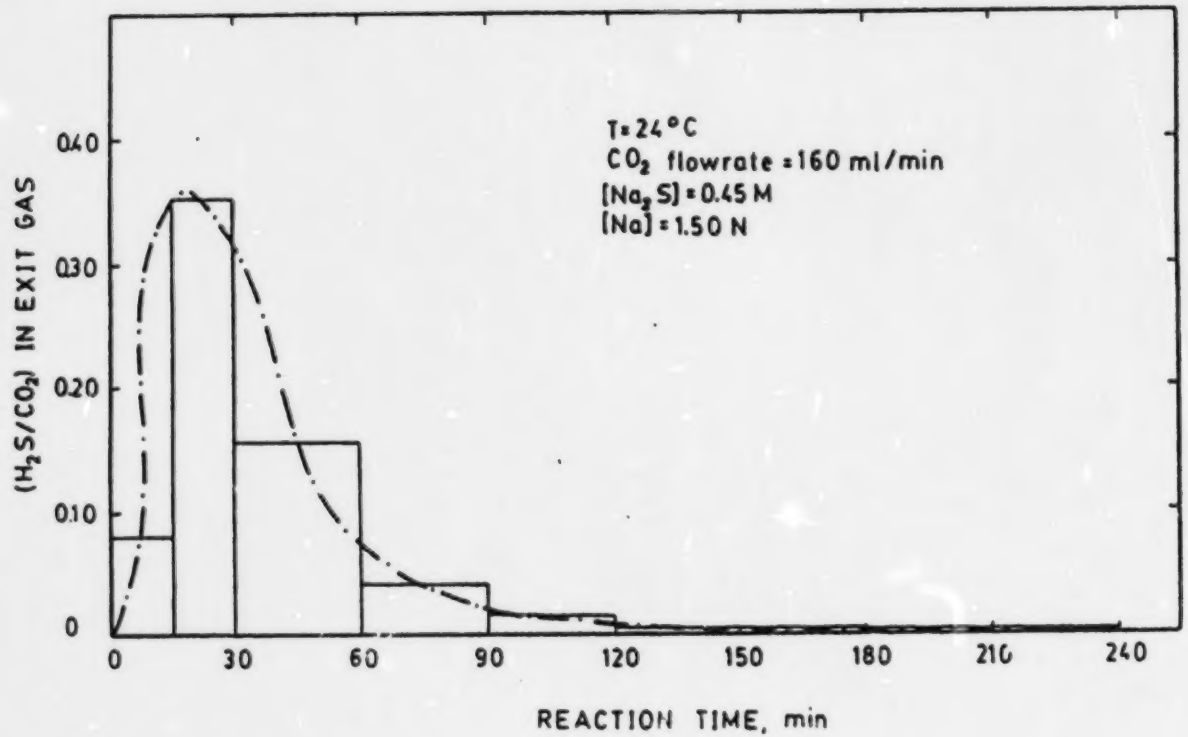


Fig. 16 Dependence of H_2S/CO_2 ratio on time of reaction.

8.8 Effect of Residence Time

It is also important to note the effect of increase in residence time. This is provided by the experiment with three reactors. Since the volume of reactants (300 ml) is double the volume in other experiments, it is a good approximation that the residence time of the gas is about twice that in the rest of the experiments.

The results are shown in Table 4. It is important to note that the average H_2S content (averaged over 2 hour period) is about twice that with a single reaction. This is due to both an increase in the amount of H_2S going out as well as decrease in the amount of CO_2 going out (consumed in the reaction). This is in spite of the fact that the average conversion decreased (84.4% with three reactors, as compared to 89.5% in single reactor equipment), see Table 5.

It may therefore be suggested that by using a larger reactor or by recirculating the H_2S-CO_2 mixture, it should be possible to obtain gas with $\%H_2S$ close to the equilibrium.

8.9 Effect of CO_2 Flow Rate

One set of experiments was performed by passing CO_2 through the reaction solution at a very high rate of 800 ml/min. (no prebubbling) i.e. 5 times the usual rate of 160ml/min. In another set of experiments, CO_2 was passed at 118 ml/minute for 2 hours. The comparative results are shown in Table 6.

The % conversion (%X) increases tremendously when high flow rate is used. At 800 ml/min. it is seen that over 87% conversion is attained within only 30 minutes (without pre-bubbling). This result is even more dramatic, when one takes into account the fact that after 75% conversion, the rate of reaction decreases significantly. However, the mean $\%H_2S$ which is a measure of CO_2 utilization also decreases. Similarly, with 160 ml flow rate, the % conversion to H_2S was higher than with 114 ml/min.

8.10 Precipitation of $NaHCO_3$

One of the important steps in the soda based process is the recycling of soda. This requires that $NaHCO_3$ crystals be obtained from the liquor from H_2S. reactor. From our observations, it appears that this can be achieved.

After about 30 minutes of passing of CO_2, it was noticed that small white crystals had formed out of the reaction solution and settled down in the bottom. After the finish of the experiment, it could be observed that some crystals had formed even on the outside part of the dispersion tube, just where CO_2 came out. As the reaction proceeded, the amount of crystals settling at the bottom increased. The maximum volume of crystals

Table 4: Effect of gaseous residence time;

(Reaction time = 2 hours)

	Single reactor	Three reactors
Residence Time	~ 1 sec.	~2 sec.
Mean (H_2S/CO_2)	0.091	0.21
Mean % H_2S	8.7	17.0
% conversion (X)	89.5	84.4

Table 5: Variation between reactors

Reactor #	% X	%X Average Over Time	(H_2S/CO_2) Average Over Time	% H_2S Average Over Time
1	89.6	84.4	0.205	17
2	84.1			
3	79.5			

Table 6: Effect of CO_2 flow rate

CO_2 flow rate, ml/min	Reaction time, minutes	% X	Mean (H_2S/CO_2)	Mean % H_2S
160	30	39.6	0.158	13.6
800	30	87.4	0.068	6.4
114	120	59	0.085	7.8
160	120	89.5	0.09	8.3

was observed in case of experiments conducted for 4 hours, the longest experiment.

No attempt was made to separate these crystals for further examination from the reaction mixture, because it was important to make sure that all Na_2S remaining in the solution after reaction was transferred to the volumetric flask in order to determine the amount of Na_2S. But all indications are that these crystals were of $NaHCO_3$ which formed as a result of the overall reaction of H_2S generation, the sum of Reactions (10) and (11).

The solubility of $NaHCO_3$ in distilled water at room temperature is 1 mole/liter. In the presence of Na^+ from other sources, the solubility should be even lower due to common ion effect. In the absence of any other data, it may be assumed that the solubility is about the same.

For the initial concentrations used so far, the concentration of $NaHCO_3$ in the reaction solution reaches this value, when % conversion reaches about 40%. After this, all $NaHCO_3$ formed should precipitate out. It is important to note that the solutions used in these experiments are not saturated. In fact, at higher temperatures, the solubility of Na_2S goes up quite a bit, which may increase the amount of $NaHCO_3$ crystals formed due to the reaction, from a given volume of solution.

8.11 Summary

The following preliminary conclusions may be drawn from the work on generation of H_2S.

(i) The production of H_2S from Na_2S by reaction with $NaHCO_3$ is thermodynamically favoured and can be accomplished in the presence of CO_2 gas.

(ii) Kinetically, the reaction (being a gas-liquid reaction) is quite fast. Even at a low CO_2 flow rate of 160 ml/min., over 75% conversion can be reached in an hour at room temperature.

(iii) The reaction rate is low initially and then increases considerably, and then tapers off in the terminal stage. The initial rate can be raised considerably if [$NaHCO_3$] can be kept high.

(iv) It is possible to attain %H_2S in the gas high enough for the production of elemental sulphur. By increasing the residence time, this can be even further increased.

(v) An increase in CO_2 flow rate increases the speed of conversion to H_2S, but the %H_2S in the gas is lower due to dilution.

(vi) The formation of $NaHCO_3$ crystals as a byproduct is confirmed.

(vii) A continuous reactor may be visualized in which Na_2S solution is added continuously, and CO_2 flowing counter currently. By keeping the Na_2S concentration high, the $\%H_2S$ in the exit gas may be maintained constantly at a high value.

9. KINETICS OF GENERATION OF H_2S AND ITS DEPENDENCE ON TEMPERATURE AND FLOW RATE OF CO_2

9.1 Experimental Procedure

About 330 g of Fisher Scientific reagent grade $Na_2S.9H_2O$ crystals were dissolved in distilled water and made up to 1 litre to obtain a concentrated stock solution. The exact concentration was determined by iodometric titration with KIO_3 and the excess KIO_3 was back-titrated by $Na_2S_2O_3$.

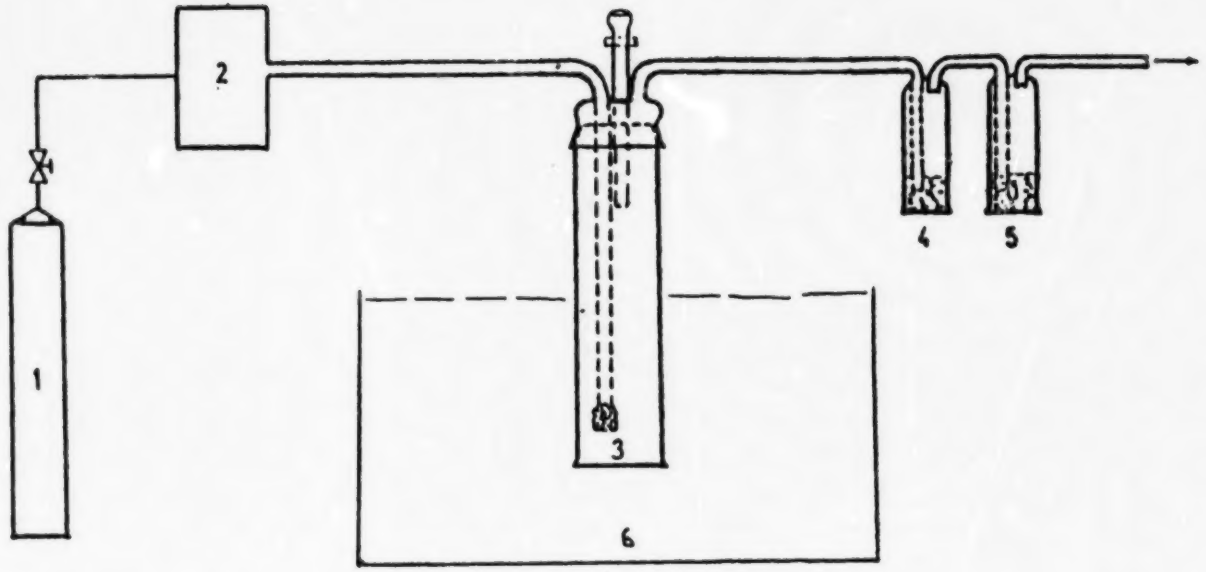
Fifty ml of this stock solution was put in a water bath 20 minutes before the start of the reaction to equilibrate to reaction temperature. One hundred ml of a 0.9 M $NaHCO_3$ solution was transferred to a reaction bottle and prebubbled in the water bath for 20 minutes before the 50 ml preheated Na_2S solution was added.

Several concentrated Na_2S stock solutions were prepared and consumed in the experiments. Special attention was called for in trying to get identical concentrations, but due to the fact that $Na_2S.9H_2O$ crystal is deliquescent, the concentrations of Na_2S stock solutions were between 1.22 and 1.33 M.

The experimental setup is shown in Figure 17. volume flow rate of CO_2 gas was accurately controlled by a Matheson controller. CO_2 gas was delivered from the dispersion tube as fine bubbles with diameters less than 2 mm. The temperature of the water bath was controlled to within 0.5°C using a Brinkmann circulator (Model IC-2).

After the predetermined time of reaction CO_2 flow was stopped. The reacted solution was immediately transferred to a 1 litre volumetric flask and diluted to the mark, so that any further reaction would be minimized. Twenty-five ml of this diluted solution was titrated right away with excess KIO_3 after the addition of dilute HCl. Attention was paid and a special apparatus was used (burette tip equipped with inner $\bar{S}24$ joint to stopper the titration flask during the course of titration) to minimize the loss of H_2S gas an I_2. The excess KIO_3 was back-titrated with $Na_2S_2O_3$ to a slight yellowish colour before starch indicator was added. The solution was then titrated to the disappearance of the purple colour.

The amount of Na_2S remaining in solution determined by iodometric titration was used to calculate the extent of reaction. Percentage covnersions at different experimental conditions are listed in Tables 7 and 8.



1 - CO_2 cylinder
2 - Mass flow controller
3 - Reaction bottle
4 - Sodium nitroprusside
5 - $AgNO_3$ solution
6 - Hot bath

Fig. 17 Experimental set-up for H_2S generation.

Time(min)	25°C	35°C	45°C	55°C
15	19.8	18.4	17.7	16.0
30	59.8	55.8	52.4	50.0
45	78.9	74.0	70.8	67.7
60	88.5	86.3	83.5	79.8
90	96.5	95.4	93.9	90.9
120	97.8	97.4	96.7	95.6
180	98.2	98.2	98.1	97.9

Table 7. % Conversion of Na_2S to H_2S at different temperature.(CO_2 flow rate 176ml/min,[Na_2S]=.43M, [Na]=1.5F, pre-bubbled 20 min)

	CO_2 Flow rate (ml/min)				
Time(min)	176	200	300	400	500
5	\	\	\	10.6	21.5
6	\	\	4.3	\	\
10	\	4.3	27.7	44.8	57.4
15	18.4	24.4	50.0	67.9	79.4
30	55.8	61.5	83.9	92.9	96.3
45	74.0	81.8	94.5	97.2	98.6
60	88.3	90.3	97.6	98.5	98.6
90	95.4	96.9	\	\	\

Table 8. % Conversion of Na_2S to H_2S at different CO_2 flow rate.(At 35°C, [Na_2S]=.43M, [Na]=1.5F, pre-bubbled 10 min)

9.2 Results

Data listed in Tables 7 and 8 are plotted in Figures 18 and 19, respectively. It is clear that the kinetics of H_2S is not strongly dependent on reaction temperature. The behaviour of the system at 35°C is similar to that at 24°C with respect to the effect of flow rate of CO_2 when the bubble size was more or less controlled. The concentrations of H_2S in the exit gas, averaged over a period of reaction time, are shown in Tables 9 to 13. With the increase of flow rate of CO_2, at 35°C, the kinetics of Na_2S conversion is faster and the peak of H_2S concentration in the exit gas appears earlier but is of lower value. The effect of CO_2 flow rate on kinetics at 35°C is similar to that observed at 24°C, outlined in Section 8.

Fig. 18 CONVERSION OF Na_2S TO H_2S AT DIFFERENT TEMPERATURE

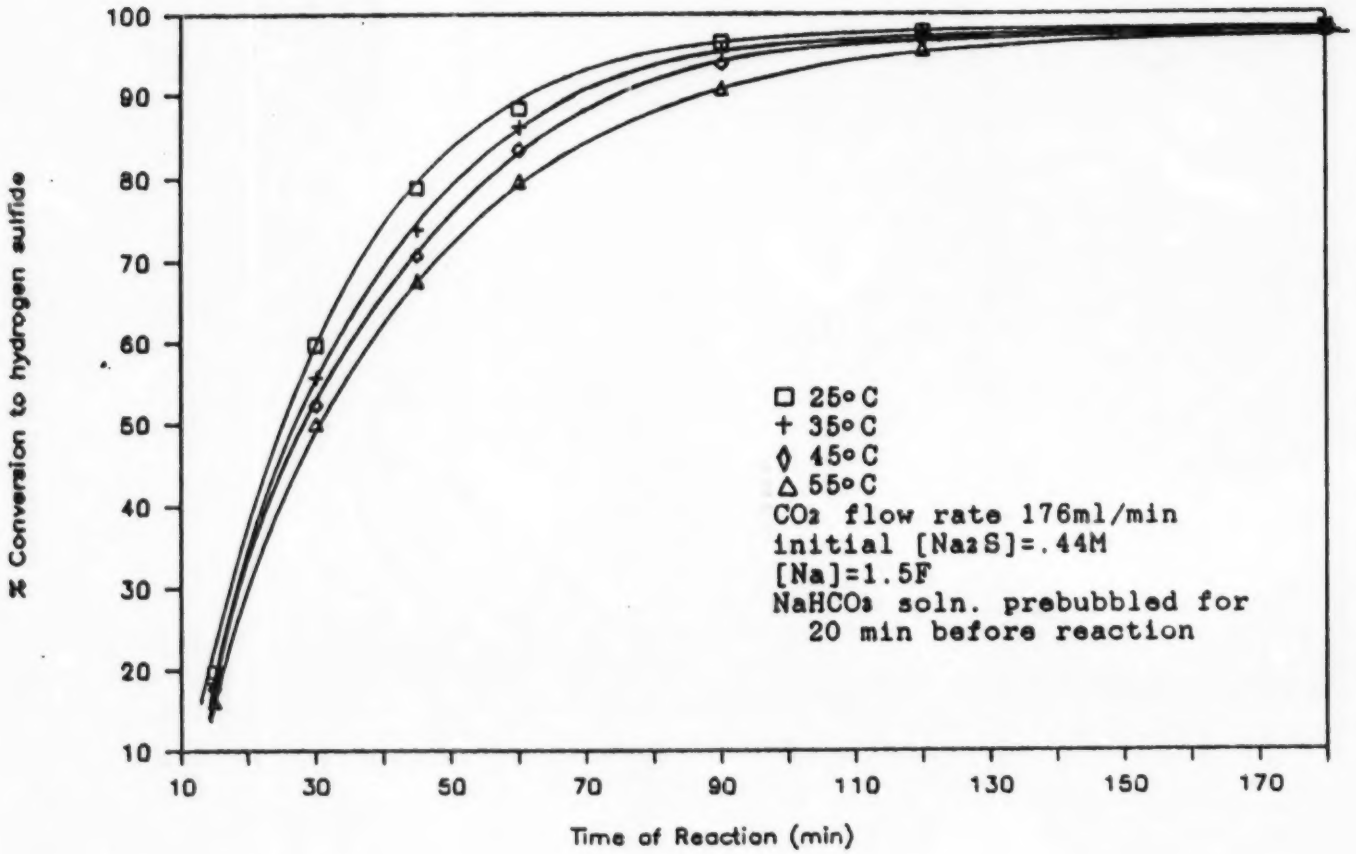
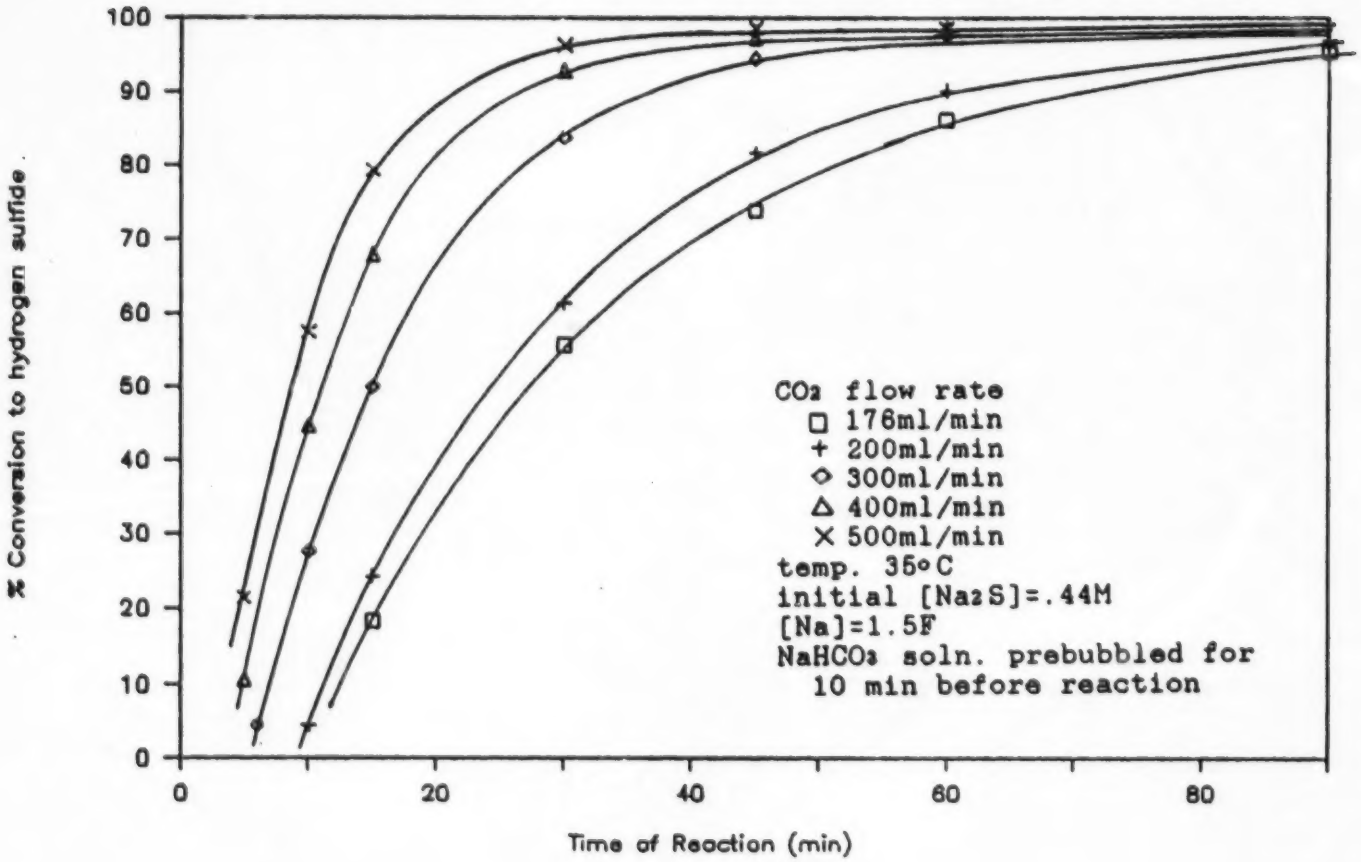


Fig. 19 CONVERSION OF Na_2S TO H_2S AT DIFFERENT CO_2 FLOW RATE



Time (min)	amount H_2S (mole)	mean % H_2S in exit gas
0 - 15	.0115	11.3
15 - 30	.0235	25.9
30 - 45	.0114	11.1
45 - 60	.0077	7.3
60 - 90	.0057	2.6

Table 9. Variation of mean % H_2S in exit gas with reaction time, with a CO_2 flow rate of 176 ml/min . (temp. 35°C, initial [Na_2S]=.44M, [Na]=1.5F, $NaHCO_3$ soln. prebubbled for 10 min before reaction)

Time (min)	amount H_2S (mole)	mean % H_2S in exit gas
0 - 10	.0027	3.2
10 - 15	.0126	41.3
15 - 30	.0233	21.9
30 - 45	.0127	10.9
45 - 60	.0053	4.3
60 - 90	.0043	1.7

Table 10. Variation of mean % H_2S in exit gas with reaction time, with a CO_2 flow rate of 200 ml/min . (temp. 35°C, initial [Na_2S]=.44M, [Na]=1.5F, $NaHCO_3$ soln. prebubbled for 10 min before reaction)

Time (min)	amount H_2S (mole)	mean % H_2S in exit gas
0 - 6	.0027	3.6
6 - 10	.0147	39.5
10 - 15	.0140	27.6
15 - 30	.0213	12.3
30 - 45	.0067	3.5
45 - 60	.0020	1.0

Table 11. Variation of mean % H_2S in exit gas with reaction time, with a CO_2 flow rate of 300 ml/min . (temp. 35°C, initial [Na_2S]=.44M, [Na]=1.5F, $NaHCO_3$ soln. prebubbled for 10 min before reaction)

Time (min)	amount H_2S (mole)	mean % H_2S in exit gas
0 - 5	.0067	8.3
5 - 10	.0215	33.1
10 - 15	.0145	20.2
15 - 30	.0157	6.4
30 - 45	.0027	1.0
45 - 60	.0008	0.3

Table 12. Variation of mean % H_2S in exit gas with reaction time, with a CO_2 flow rate of 400 ml/min . (temp. 35°C, initial [Na_2S]=.44M, [Na]=1.5F, $NaHCO_3$ soln. prebubbled for 10 min before reaction)

Time (min)	amount H_2S (mole)	mean % H_2S in exit gas
0 - 5	.0135	14.3
6 - 10	.0225	26.4
11 - 15	.0138	14.7
16 - 30	.0106	3.4
31 - 45	.0014	1.4
46 - 60	.0000	0.0

Table 13. Variation of mean % H_2S in exit gas with reaction time, with a CO_2 flow rate of 500 ml/min . (temp. 35°C, initial [Na_2S]=.44M, [Na]=1.5F, $NaHCO_3$ soln. prebubbled for 10 min before reaction)

10. CONCLUSIONS

Based on experimentation and computation in our laboratory in the last twelve months, the following conclusions may be reached:

(i) Carbothermic reduction of sulphides of common metals by coal, in the presence of a basic oxide, can be carried out under conditions of industrial significance.

(ii) Soda is a better flux than lime in carbothermic reduction for both thermodynamic and kinetic reasons.

(iii) Na_2S can be converted to H_2S at ambient temperature and atmospheric pressure at very high reaction rate with the exit gas, in a continuous reactor, to be CO_2 - 25% H_2S.

(iv) A new process, noted for its simple, economical and effective way of converting H_2S/CO_2 mixture to CO_2 for recycling and elemental sulphur, has been announced by a Japanese company.

APPENDIX I

CARBOTHERMIC REDUCTION OF SULPHIDE ORE BY COAL IN THE PRESENCE OF BASIC OXIDES

Our results of a pyrometallurgical study by using a crucible made of steel in a tubular furnace which is heated electrically, are documented. A schematic diagram is shown in Figure 1.

Three pairs of experiments, all at 950°C, have been carried out. A crucible containing pre-mixed powdery raw materials (for composition see Tables 1(A) and 1(B)), was introduced to the hot zone at 950°C, under a gentle flow of inert gas, and considered to be time zero. The extent of completion of reaction is assessed by weight loss due to the formation of carbon monoxide in the reduction of sulphide ores. Based on weight loss data the computed results are given in Tables 2(A) and 2(B). Assumptions made in computations are listed as footnotes in Tables 2(A) and 2(B).

From Table 2(B), one may reach the following qualitative conclusions:

(1) On a molar basis, sodium oxide is more effective than calcium oxide.

(2) A large amount of excess of basic oxides or carbon may not be necessary.

(3) A large temperature gradient exists in the system during the course of experiments.

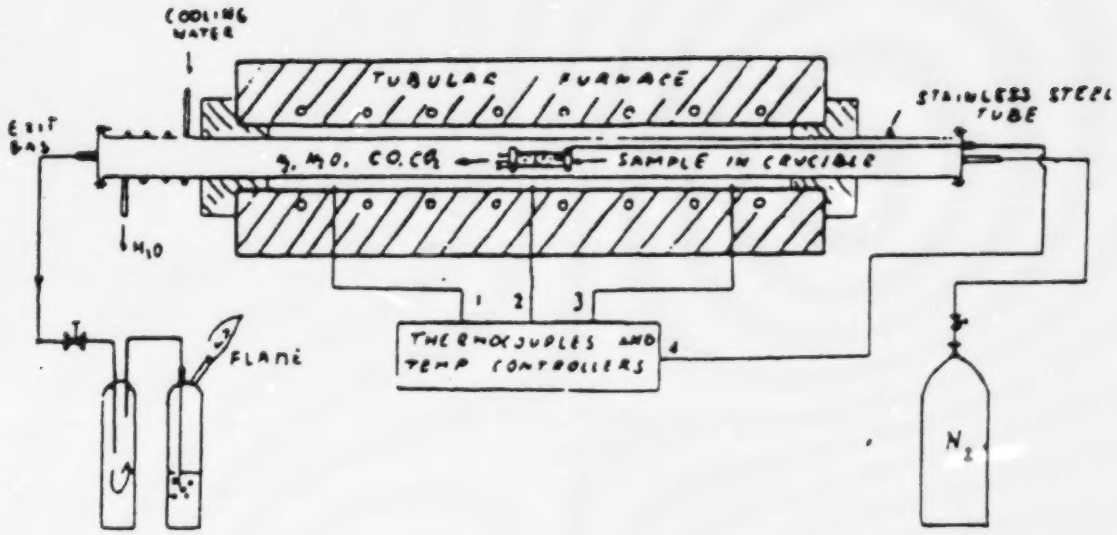


Fig. 1 Schematic diagram of the experimental apparatus.

Table 1 (A) Composition of raw materials (wt. %)

Mineral	Fe	Cu	S	SiO_2	CaO	Ni	Na_2O	CO_2	C_{Fix}	Volatile Matter	Others
Chalcopyrite	29.65	29.1	33.4	2.60	0.3	0.69	-	-	-	-	4.16
Lime	-	-	-	-	95.0	-	-	-	-	-	5.0
Na_2CO_3	-	-	-	-	-	-	57.9	41.1	-	-	1.0
Coal	-	-	0.6	3.0	-	-	-	-	65.0	28.4	3.0

Table 1 (B) Composition of green mixtures (before reduction) (wt. %)

Exp. No.	Fe	Cu	S	SiO_2	CaO	Ni	Na_2O	CO_2	C_{Fix}	Volatile Matter	Others
1 and 2	17.05	16.73	19.25	1.72	33.42	0.38	-	-	4.85	2.13	4.37
3 and 4	16.45	16.15	18.60	1.77	32.00	0.38	-	-	7.03	3.08	4.33
5 and 6	15.07	14.80	17.05	1.62	23.50	0.35	8.47	6.02	6.47	2.83	3.80

Table 2 Composition of reduced mixtures by material balance$ after reduction at 950°C.

(A) Composition in wt. %

Exp. No.	S:CaO:Na_2O:C Molar Ratio	Time of Reduction (min.)	Fe	Cu	Na_2S	CaS	S*	CaO	C	SiO_2	Ni	Others
1	1:0.99:0:0.67	25	19.22	18.86		26.57	9.89	17.0	1.03	1.93	0.43	4.92
2	1:0.99:0:0.67	30	19.51	19.14	-	30.78	8.35	14.28	0.42	1.96	0.44	5.00
3	1:0.99:0:1.01	25	18.90	18.56	-	29.25	8.37	14.02	3.20	2.03	0.44	4.98
4	1:0.99:0:1.01	30	19.50	19.15	-	38.42	4.98	8.06	1.94	2.10	0.45	5.14
5	1:0.78:0.26:1.01	25	19.12	18.79	13.52	27.95	3.68	8.08	1.47	2.05	0.44	4.82
6	1:0.78:0.26:1.01	30	19.28	18.94	13.63	30.20	2.80	6.42	1.14	2.07	0.45	4.86

S*: Sulphur remaining as sulphides of Cu and Fe.

In the presence of basic oxides CaO and Na_2O, the reduction of sulphides is chiefly according to the following chemical reaction:

$$CuFeS_2 + \underset{2Na_2O}{2CaO} + C \rightarrow Cu + Fe + \underset{2Na_2S}{2CaS} + CO(g) \qquad (1)$$

$ Material balance was computed based upon reaction (1) and the following assumptions:

(i) Carbon is oxidized only to the CO stage.

(ii) The volatile matter from the coal does not take part in the reaction, as it is liberated at low temperature. Similarly, it is assumed that the CO_2 from the decomposition of Na_2CO_3 does not take part in any reaction.

(iii) The thermodynamically stabler Na_2S is formed in preference to CaS.

Table 2 (B) Extent of Conversion$$

Exp. No.	S:CaO:Na_2O:C Molar Ratio	Time of Reduction (Min.)	% Conversion	% Carbon Utilization
1	1:0.99:0:0.67	25	54.4	81.1
2	1:0.99:0:0.67	30	62.1	92.4
3	1:0.99:0:1.01	25	60.8	60.4
4	1:0.99:0:1.01	30	77.4	76.8
5	1.0.78:0.26:1.01	25	83.0	82.0
6	1:0.78:0.26:1.01	30	87.2	86.1

$$ Extent of conversion is defined as the fraction of sulphur converted to sulphides of lime and sodium; therefore, % conversion

$$\% \text{ Conversion} = \left(1 - \frac{S^*}{S_{Total}}\right) \times 100$$

% Carbon Utilization is calculated as:

$$\left(1 - \frac{\text{Amount of carbon in the mixture after reduction}}{\text{Amount of carbon in the mixture before reduction}}\right) \times 100$$

APPENDIX II

RECOMMENDED PROCESS FOR THE CONVERSION OF H_2S IN H_2S/CO_2 MIXTURE TO ELEMENTAL SULPHUR AND CO_2 FOR RECYCLING

EFFLUENT GAS TREATMENT SYSTEM BY BIOENGINEERING

by Kanji Ohida

(published in Japanese in "Chemical Equipment and Technology and Implementations", May Issue, 1986)

Removal of H_2S is concerned with petroleum, coke oven, natural gas and geothermal power plants. Methane fermentation gas, which is a leading bio-mass-energy requires removal of H_2S. The H_2S of extra low concentrations is a source of rank odor which has demanded a variety of facilities for H_2S removal. Current removal methods consist of dry and wet methods. The dry method is for the removal of extra low concentration and odor in which absorbent and active carbon are used including iron oxides. The wet method is, in turn, classified into two groups. One is to absorb H_2S with potassium carbonate and ethanol amine, to separate H_2S by stripping and to carry out oxidation treatment of sulphur by Klaus Process. The other is the one in which a direct production of sulphur from the oxidation of H_2S absorbed, using alkali aqueous solution.

Though these techniques have been well established, the following disadvantages are also known:

(1) Degradation of absorbents and catalyses.

(2) Loss of absorbent solutions by side reactions and equipment troubles.

(3) Selectivity of CO_2.

(4) Pressurization and heatings are required.

(5) Corrosiveness of abosrbent solutions.

This company has developed a new technology in which $Fe_2(SO_4)_3$ is used as an absorbent and its reformation is by use of the microbes.

1. Characteristics and Principles

This is a wet desulphurization in which $Fe_2(SO_4)_3$ is used and the sulphur is recovered. Fig. 1 is its flowsheet.

In the absorbing tank, the raw gas is washed and H_2S is absorbed and oxidized, thus producing elemental sulphur. $Fe_2(SO_4)_3$ is reduced to $FeSO_4$ with the following equation:

$$H_2S + Fe_2(SO_4)_3 = S^o + 2FeSO_4 + H_2SO_4$$

In this case, a side reaction such as a formation of thio-hydrosulphate does not necessarily follow.

Bioreactor-Based H_2S Treatment System Marketed

NKK has reached an agreement with Dowa Mining Co., Ltd. on a marketing strategy for a bioreactor-based hydrogen sulfide (H_2S) treatment system developed by Dowa Mining. Under the agreement, the system will be marketed by both NKK and Dowa Mining, but total plant engineering and all other operating rights will reside solely with NKK. This will enable NKK's engineering and business capabilities to be effectively linked with the technical expertise of Dowa Mining, a link that will allow both companies to develop demand in a wider range of fields and to provide well-organized support services.

The new treatment system uses bacteria called thiobacillus ferrooxidans to treat hydrogen sulfide gases. The hydrogen sulfide in the incoming sour gas is absorbed by a ferric sulfate solution in an absorber. The absorbed H_2S is then oxidized to elemental sulfur while the ferric sulfate is converted into ferrous sulfate. A sulfur separator is used to separate the elemental sulfur by dewatering, and the absorbing solution containing ferrous sulfate is oxidized and regenerated into ferric sulfate by the bacteria in the bioreactor, after which it is circulated back to the absorber.

Perhaps the most outstanding feature of the new system is its low operating cost: It can be run at one-half to one-third the cost of conventional H_2S treatment systems.

The low running cost is the result of several advancements that the system brings to the field of H_2S treatment. It does not require a catalyst or special chemicals, and, because it does not generate side reactions, there is no degradation of the absorbent. Moreover, energy costs are minimal, since the reactions occur at ambient temperatures and at atmospheric pressures, which also makes for safe, stable operations and easier maintenance.

An additional benefit of the new system is the fact that it does not generate any effluent, so there is no need for costly waste-water treatment equipment, and the system's high H_2S selectivity under coexistence with carbon dioxide also contributes to reducing treatment costs.

This unique bioreactor-based H_2S treatment system has a wide range of potential applications, including the treatment of chemical plant exhaust gas, the recovery of sulfur from amine off-gas, the desulfurization of sludge digested gases at sewage treatment plants, and the treatment of geothermal-power-generation tail gas.

To demonstrate the system's suitability for these and other applications, NKK carried out a demonstration test using a mini-plant to treat various gases at a domestic refinery. During the test, the mini-plant was stably operated for two weeks, treating both sour and acid gases.

A full-scale version of the new system is now in operation at the Kosaka Works of Barium Chemicals Co., Ltd. in Akita Prefecture. It is being used to recover sulfur from gases generated in the barium salt-production process. Since going on stream in 1984, the Akita facility has continued to operate smoothly, recovering about five tons of sulfur a day.

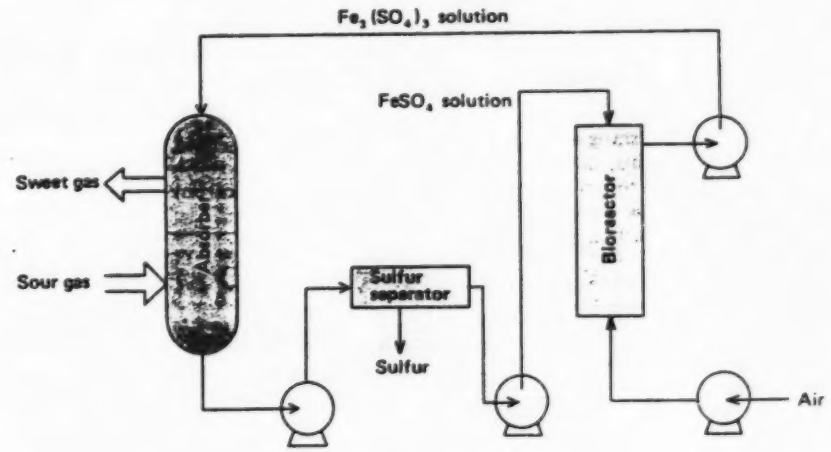
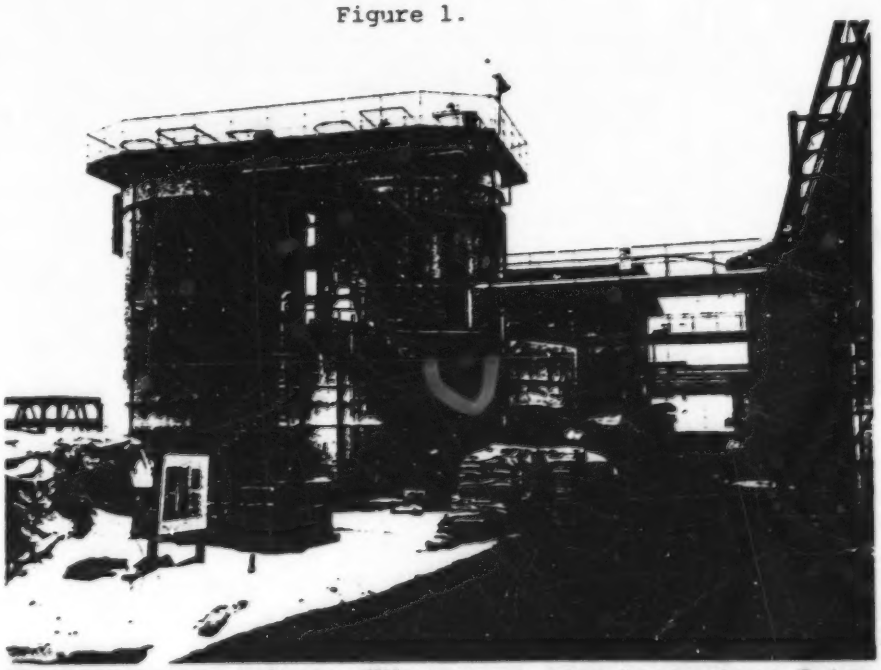


Figure 1.



The bioreactor-based hydrogen sulfide treatment system in operation at Barium Chemicals' Kosaka Works in Akita Prefecture

NK-EXA

(Continued from Page 2)

plans for the introduction of computers and their operation to developing management and software programs, (4) CAD/CAM technology services, utilizing the high-level expertise that NKK has acquired through its shipbuilding activities; (5) AI (artificial intelligence) services, based on NKK's experience in steel making, and (6) VAN (value added network) activities, which involve large computers and digital network nationwide.

Elemental sulphur is dehydrated and separated. The absorbent in the form of $FeSO_4$ is placed in the reformation tank and is oxidized to $Fe_3(SO_4)_3$ by thiobacillus ferro-oxidans (TBFO), thus recycled to the system. The equation is as follows:

$$2FeSO_4 + H_2SO_4 + 1/2\ O_2 = Fe_2(SO_4)_3 + H_2O$$

Characteristics of the desulphurization are as follows:

(1) As the absorbent is acidic, there is a tendency for selectivity of CO_2.

(2) Since only $Fe_3(SO_4)_3$ which is a pure inorganic salt is used as an absorbent, no byproduct is formed and no degradation of absorbent takes place.

(3) The process proceeds under an atmospheric pressure and an ambient temperature and recovery of sulphur is easy.

(4) The reformation of absorbent is performed by microbes and the cost is remarkably reasonable.

(5) Wet gas is treated as it is.

2. Thiobacillus Ferro-oxidans (TBFO)

TBFO are microbes which reside in an effluent in mines, especially of sulphide minerals. In general, microbes are divided into two categories depending on whether they take organic or inorganic substances as a source of their energy and nutrition. The former is a majority and the latter a minority, to which the TBFO belongs.

The TBFO is a favourable habitat in a strong acidic effluenct of pH 2 to 3. Energy is generated when ferrous ions are oxidized to ferric ions. Only CO_2 in the air is used to make up cells, which means the formation of organic substances out of inorganic substances. The oxidation reaction is as follows:

$$2FeSO_4 + H_2SO_4 + 1/2\ O_2 = Fe_2(SO_4)_3 + H_2O + 17\ kcal.$$

This reaction is extremely slow; however, with the TBFO the reaction rate is accelerated as fast as 500,000 times.

The TBFO is of a short rod shape of 0.5 x 1.0 μm, and reproduces by division. A temperature range of 20 to 30° is adequate for their habitat. since they live in mines, they are resistant to strong acids up to pH = 1. In the presence of heavy metal ions such as Cu, Zn, Ni, Co, Mn, Cr, Cd, etc., oxidation of Fe^{2+} and reproduction by division are not disturbed. However, a higher concentration of U, Mo, and Sn disturbs their survival. Ag and Hg are very harmful to their living. Halogen ions are also harmful in a higher concentration. Organic substances are, in general, harmless.

3. Utilization of TBFO

The TBFO is utilized in mining, includingbacteria leaching and mine effluent treatment. Bacteria leaching in mining of copper and uranium is common in North America. For example, the USA produces 10 to 20% of copper by this method.

Mine effluent treatment with the TBFO has been developed by this company. This technology enables the treatment of strong acidic and high iron concentrate effluents. The latter is a pretreatment in which iron ions are oxidized so as to effect efficiently the downstream processes of "neutralization" and sedimentation at a lower cost.

APPENDIX III

THERMODYNAMICS AND MASS BALANCES OF THE TREATMENT OF CaS WITH HCl

(A) Thermodynamic Calculations for HCl Treatment

(i) Treatment with HCl

In the aqueous medium, the reaction between CaS and HCl is:

$$CaS_{(s)} + 2H^{+}_{(aq)} \text{ ----> } Ca^{+2}_{(aq)} + H_2S_{(g)} \qquad (1a)$$

T, ^{o}K	ΔG^{o} , Kcal/mole
298	- 28.0
373	- 27.7

$$\Delta G^{o} = -RT \ln ({}^{P}H_2S)\ (a_{Ca}{}^{+2})/(a_{H}{}^{+})^{2} \qquad (1b)$$

In order to generate HCl in the second reactor, $[Ca^{+2}]$ should be high. The solubility limit of $CaCl_2$ in cold water = 6.71 mole/liter, and 14.3 mole/liter in hot water[1]. For a concentration of $CaCl_2$ (say, 6 moles/liter) and assuming that (a) the dissociation of $CaCl_2$ is 100%; and (b) the activity co-efficient is reasonably constant, $a_{Ca}{}^{2+} \simeq [Ca^{+2}] = 6$.

For a final pH of 6.9, $[H^{+}] = 10^{-6.9}$, the equilibrium ${}^{P}H_2S$, from (6) is:

$$({}^{P}H_2S)^{eq}_{298} = 9.08 \times 10^{5} \text{ atm.}$$

Thus, generation of H_2S gas is not a problem.

(ii) HCl Generation

The product of Reactor I is treated with CO_2 gas. The concerned reaction is:

$$Ca^{+2} + H_2O + CO_{2(g)} \text{ ----> } 2H^{+}_{(aq)} + CaCO_{3(s)} \qquad (2a)$$

T, ^{o}K	ΔG^{o} , Kcal/mole
298	+ 13.8
373	+ 16.2

At equilibrium,

$$\Delta G_{o} = -RT \ln [a_{H}{}^{+}]^{2}/[a_{Ca}{}^{++}]\ P_{CO_2} \qquad (2b)$$

Assumption: $[Ca^{+2}]_{final} \simeq [Ca^{+2}]_{initial}$. Operation of the reactor at a high CO_2 pressure, say, 100 atm., enables one to obtain a high pH value (calculated from Eq. (8)).

T, °K	Initial [Ca+2] moles/l	P_{CO_2} atm.	Equilibrium pH
298	6	100	3.6
373	14	100	3.17

The final [Ca+2] may be calculated from stoichiometry for Eq. (7).

$$[Ca^{+2}]_{final} = [Ca^{+2}]_{initial} - 1/2[H^+]$$

At 298°K, $= 6 - 1/2 \times 10^{-3.67} = 5.9998 \simeq 6$ moles

Hence, the assumption is justified.

(B) Mass Balance When Reactors I and II are Operating in Steady State

The most important constituent of the reduction mixture being treated is CaS. Hence, the calculations are carried out, per mole of CaS being treated. The other constituents of the reduction mixture are not mentioned.

Conditions for Reactor I:

At steady state, all the HCl required for the process is in the liquor coming in from Reactor II. At 298°K the pH assumed is 3.67, the maximum possible from thermodynamic calculations. The liquor going out from Reaction I is assumed to have a pH of higher than 6, in which case, the amount of HCl going out is negligible.

Per mole (72 grams) of CaS to be treated, from Reaction (1a), 2 moles of H^+ is required. If the reactor operates at 298°K, the amount of $CaCl_2$ in the liquor = 9,400 l x 6 moles/l x $111/10^6$ tonnes/mole = 6.25 tonnes.

If operated at 373°K:

Initial pH = 3.17 Amount of liquor = 2.98 m^3

Amount of $CaCl_2$ at $[CaCl_2]$ of 14 moles/l = 2.98 x 14 x $111/10^6$ = 4.63 t

Conditions for Reactor II:

At 298°K Input:

Incoming liquor: 9.4 m^3 H_2O + 6.25 t $CaCl_2$ from Reactor I, per mole of CaS.

H_2O: 1 mole/mole CaS = 18 ml/mole of CaS

CO_2: 1 mole/mole CaS = 22.4 Nl at 100 atm. pr.

Output:

Outgoing liquor: 9.4 m^3 H_2O at pH of 3.67 + 6.25 t $CaCl_2$

100 grams of $CaCO_3$

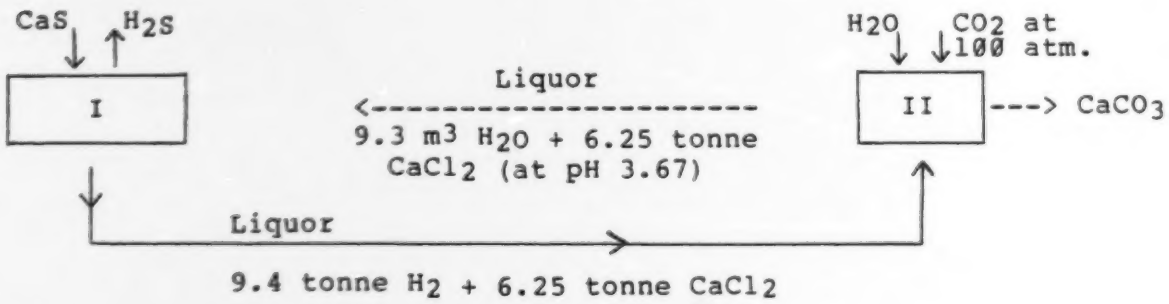


Figure 1: Schematic diagram and mass balance for HCl treatment.

Net Reaction of I and II

$$CaS + H_2O + CO_{2(g)} \longrightarrow CaCO_3 + H_{2S(g)}$$

I II II I I